

Book of abstracts



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31st European Crystallographic Meeting

Plenary Lectures

PL-O1

Crystallography in the 21st century: the age of electron?

Lukáš Palatinus

 Department of Structure Analysis, Institute of Physics of the CAS, Prague, Czech Republic

email: palat@fzu.cz

Crystallography as a scientific discipline has a history reaching at least four hundred years in the past. However, only in the 19thcentury it became a systematically studied field. In these early times, crystals were studied mostly by visible light. This "age of light" ended abruptly with the discovery of the diffraction of X-rays by crystals, starting the "age of x-rays" and the dramatic development of structural crystallography.

Electron microscopy and electron diffraction have long been considered useful, but mainly supplementary crystallographic techniques. However, we have been witnessing a number of important developments in the field of electron crystallography over the last decade that have changed the situation. First, it is the wide-spread availability of aberration-corrected transmission electron microscopes now allows a routine observation of – mostly inorganic – crystals at atomic resolution, including atomic-level chemical analysis. This gives an unprecedented insight into the structural arrangements at the smallest possible scale. Second, the development of the Cryo-EM technique for the reconstruction of molecular structures by high-resolution single-particle imaging brought a qualitative leap forward in our ability to understand the structures of biologically relevant molecular systems.

Somewhat in the shadow of these two ground-breaking developments stands another important progress in electron crystallography, namely the ability to solve and refine crystal structures from electron diffraction data. While some ten years ago an ab-initio solution of a crystal structure purely from electron diffraction data was limited only to special cases and was considered a very difficult challenge, today it has become an almost routine procedure. Hundreds of crystal structures have been solved from electron diffraction data, and some of them refined to accuracy comparable to the accuracy of x-ray structure analysis. The examples cover all types of structures, from oxides and metal alloys through minerals, zeolites and other framework materials, to metal-organic frameworks, organometallic compounds or pharmaceutically relevant organic materials, and even macromolecular crystals. This technique opens up a whole new realm of application of single-crystal structure analysis, because electron diffraction techniques are able to analyze crystals down to the size of a few nanometers.

There is no doubt that in the coming years x-ray diffraction techniques will remain dominant in the crystallographic research. However, seeing the rapid growth of importance of electron-based techniques, one may indeed ask a question: After the 19th century being the age of light and the 20th century being the age of rays, is the 21st century going to be the age of electrons?

Keywords: electron crystallography, electron microscopy, nanocrystals

PL-O2

A tale in two parts: how a search for antivirulence compounds led to the discovery of a shapeshifting copper resistance protein

Jennifer Martin¹

1. Griffith Institute for Drug Discovery, Griffith University, Nathan, Australia

email: jlm@griffith.edu.au

Protein disulfide bonds are covalent links formed between sulfurs of cysteine sidechains. There is now overwhelming evidence to show that these inter-residue bonds are critical for Gram negative bacterial virulence [1]. This presentation describes how the structures of the bacterial machinery components that introduce disulfide bonds into folding proteins [2] have been used in the search for inhibitors [3,4,5]; and outlines the serendipitous discovery of a shape-shifting foldase [6] that is potentially useful for plug-and-play bionanotechnology.

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Keywords: bionanotechnology, anti virulence compounds

Keynote Lectures

KN-1

The vocabulary of protein-DNA interactions: Symmetry, degeneracy, modifications

Matthias Bochtler¹

 International Institute of Molecular and Cell Biology & Institute of Biochemistry and Biophysics, Warsaw, Poland

email: mbochtler@iimcb.gov.pl

The basics of protein nucleic acid interactions have been worked out a long time ago, but new themes are still emerging. The vocabulary for the non-degenerate recognition of DNA bases is well understood, but this is not the case for semi-degenerate recognition, which may occur "accidentally", or be imposed by symmetry. In the first part of my talk, I will focus on principles of semi-degenerate readout of DNA sequence, by minor groove readout, base unstacking, and nucleotide flipping (1). In the second part of my talk, I will concentrate on modification specific DNA binding. How nucleic acid modifications such as methylation inhibit DNA binding by steric exclusion is readily understandable. Whether a predicted clash is biologically relevant depends on whether protein and nucleic acid are sufficiently flexible to avoid the steric conflict (2). How nucleic acid conformations become a prerequisite for binding is harder to understand, especially when the dependence on the modification is stringent and when a modifier group (such as a methyl group) offers little opportunity for strong attractive interactions. In my talk, I will focus on several published and unpublished structures from our own work which illustrate the modification selective binding of nucleic acids containing 6-methyladenine, 5-methylcytosine (5mC), 5-hydroxymethylcytosine (5hmC), and glucosyl-5-hydroxymethylcytosine (g5hmC) (3).

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Keywords: Symmetry, degeneracy, modifications

KN-2

The Joy of Seeing - in honour of Dorothy Hodgkin

Eleanor Dodson1

1. University of York, York, United Kingdom

email: eleanor.dodson@york.ac.uk

To quote Dorothy Hodgkin: The great advantage of X-ray analysis as a method of chemical structure analysis is its power to show some totally unexpected and surprising structure and to do so with absolute certainty.

I will show examples of how Fourier analysis using X-ray observations from a crystal, combined with imperfect phases, can allow us to boot-strap our way to a satisfactory structure. Combining these basic principals with the great computing power, and excellent data acquisition facilities now available has extended our power to "see" to new levels.

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Keywords: Fourier analysis, computing techniques



Understanding and using likelihood in structural biology

Randy Read1, Robert Oeffner1, Airlie McCoy1

 Department of Haematology, Cambridge Institute for Medical Research, University of Cambridge, Cambridge, United Kingdom

email: rjr27@cam.ac.uk

The principle of maximum likelihood provides an ideal way to understand how experiments and prior knowledge can be used to inform our understanding of the systems we study. Likelihood-based methods now pervade all aspects of macromolecular crystallography and, increasingly, other branches of structural biology.

Compared to previous approaches, such as heuristic methods based on the properties of the Patterson function or least-squares optimisation, likelihood-based methods are found to be more sensitive and to lead to better models. Molecular replacement methods are a prime example where the application of likelihood allows structures to be determined with poorer or less complete models, partly because it provides a clear way to build up more complete solutions from multiple components.

A new understanding of the effects of measurement error [1] and of the statistical properties of crystallographic likelihood targets [2, 3] allows us to predict whether or not we will be able to place a particular model, integrating the influence of resolution limit, data quality, model completeness and model quality. This understanding led to the surprising prediction that, given data to sufficiently high resolution, molecular replacement techniques could even be used to place single atoms.

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Keywords: likelihood, molecular replacement, phasing



How CRISPR-Cas RNA-guided endonucleases cut specific DNA regions for Genome Editing?

Guillermo Montoya1

 Novo Nordisk Foundation Center for Protein Research Faculty of Health and Medical Sciences, University of Copenhagen, Copenhagen, Denmark

email: guillermo.montoya@cpr.ku.dk

Since ancestral time mankind has tried to modify plants and animals to obtain an offspring that could adapt to our needs. In this way farmers have selected more efficient animals to produce more meat, more resistant plants, faster and resistant horses or cows that produce a larger amount of milk. Our ability to modify organisms has changed dramatically with the introduction of genome editing. Thanks to the discovery of new genome modifying enzymes we can perform a safer and faster manipulation to edit a genome, thus facilitating organism redesign or the treatment of monogenic diseases and some types of cancer. I will address the molecular mechanism that control specificity and cleavage of one of these tools, Cpf1, a single RNA-guided endonuclease of class 2 type V CRISPR-Cas system, which is emerging as a powerful genome editing tool. To provide insight into its DNA targeting mechanism, we have determined the crystal structure of Francisella novicida Cpf1(FnCpf1) in complex with the triple strand R-loop formed after target DNA cleavage. The structure reveals a unique machinery for target DNA unwinding to form a crRNA-DNA hybrid and a displaced DNA strand inside FnCpf1. Our study reveals a singular working model of RNA-guided DNA cleavage by Cpf1, opening up new avenues for engineering this genome modification system.

Keywords: DNA, CRISPR, Genome editing



The roots of Quantum Crystallography

Piero Macchi1

1. Department of Chemistry and Biochemistry University of Bern, Bern, Switzerland

email: piero.macchi@dcb.unibe.ch

The term *Quantum Crystallography* has recently entered the scientific language, following a definition by Massa, Huang & Karle (1995). Their vision was quite narrow-focused, identifying quantum crystallography with the possibility of improving an electronic wave function by means of X-ray scattering intensities, or otherwise using wavefunction-based methods to improve the traditional crystal structure models.

Instead, if quantum crystallography refers to the extraction of quantum-based information from crystallographic measurements or the use of theoretical quantum chemistry to improve the quality of the crystallographic models, then it is clear that this field finds its roots directly at the beginning of modern crystallography, after the discovery of X-rays. In facts, it was only in the 1960s that this kind of studies became technically available, especially under the impulse of R. Weiss (1966), who showed how electron charge density, in position or in momentum space, could be determined from X-ray diffraction.

A terrific development occurred in the 1970s, fostered by P. Coppens (1984) and R. F. Stewart (1976) and many coworkers who paved the way to extract a huge array of quantum mechanical quantities from crystallographic experiments. The progresses have involved also the determination of magnetization densities and spine distributions (Becker, 1980), the refinement of reduced density matrices (Gillet, 2007) and the calculation of X-ray restrained wavefunctions (Jayatilaka, 1998).

Many methods to analyze those quantities have been developed and adopted, mostly based on electron density partitions and quantum topology (Bader, 1990).

These roots enable nowadays a modern and broader science, which is under development and takes advantage of improved modelling techniques, for example combining different kinds of experiments, and from the new types of source that are currently available at large scale facilities.

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Keywords: charge density, spin density, quantum mechanics, quantum crystallography, wave function refinement

KN-6

Application of advanced transmission electron microscopy techniques to structure solution and refinement of complex inorganic materials

Joke Hadermann¹

1. EMAT, Dept. Physics, University of Antwerp, Antwerp, Belgium

email: joke.hadermann@uantwerpen.be

The crystal structure solution of complex inorganic compounds, including commensurately or incommensurately modulated compounds, is often very challenging, even using the well-established methodology of single-crystal X ray crystallography. This task becomes even more difficult for materials that cannot be prepared in a single-crystal form, so that only polycrystalline powders are available. Transmission electron microscopy (TEM) has a strong advantage in such cases, as it can study separate nm sized crystallites, turning a "powder sample" into a sample with a multitude of "single crystals". A TEM furthermore allows using many different techniques, from diffraction to imaging to spectroscopy. Huge advances were made in both high resolution imaging and spectroscopy as well as electron diffraction methods over the last decade. In this lecture, an overview will be given which and how advanced transmission electron microscopy techniques can be specifically well used to aid the structure solution and refinement of complex inorganic materials, as well as the potential of some recent analysis tools and instrumentation towards this target.

Keywords: TEM, modulated, structure



Biomolecular structure determination by electron diffraction of 3D microcrystals

Brent Nannenga1

1. Chemical Engineering, Arizona State University, Tempe, United States of America

email: Brent.Nannenga@asu.edu

A common barrier to high-resolution biomolecular structure determination is the growth of large well-ordered crystals. Electron diffraction is capable of producing high-quality diffraction data from crystals that are orders of magnitude smaller than those needed for conventional X-ray crystallographic experiments, and 3D electron diffraction methods have recently begun to yield high-resolution structures from extremely small microcrystals. In this presentation, the cryo-electron microscopy technique of microelectron diffraction, or MicroED, will be described in detail along with representative structures determined by the method. Additionally, current work in our lab, which is focused on improving and extending this technique to very difficult samples, such as membrane proteins, will be presented.

Keywords: Electron diffraction, protein crystallography

KN-8

Exotic topochemical alteration of the cationic sublattices in oxides: the complex crystallography behind

Olivier Mentré¹

1. UCCS, UMR CNRS 8181, Villeneuve D'ascq, France

email: olivier.mentre@ensc-lille.fr

The possibility to modify inorganic oxides at moderate temperature, under kinetic rather than thermodynamic control leads to metastable structural rearrangements with novel electronic partitions and properties. Here we present a review of recent exotic reversible topochemical reactions studied in the lab. In most cases, the observed modidication concerns the anionic sub-array. However we have evidenced a number of structural lattices in which the cationic lattices itself may be drastically re-arranged via concomitant or not alteration of the anionic sublattice. For instance, the controlled oxidation of the 2D-ising ferromagnetic BaFe2+2(PO4)2 into Fe-depleted BaFe2/3+2-x(PO4)2 (x<0.66) leads to a series of intermediate phases with full vacancy/Fe ordering and to nanometric Fe₂O₃[1]. Here, antiferromagneticexchanges are recovered along with the Fe2+ to Fe3+ oxidation. Other pertinent examples of metal exsolution will be discussed. On the opposite, playing redox chemistry in 2D-oxides such as the multiferroic hexagonal $YMn^{3+}O_3$, $YbFe^{2.5+}O_4$ and $Yb_2Fe^{2.66+}O_7$, the metal content is maintained but drastically restacked during reduction/oxidation into YMn²⁺O_{2.5} YbFe³⁺₂O_{4.5} and Yb₂Fe³⁺₃O_{7.5} [2,3]. Generally, all transformed compounds require complex crystal-chemistry features with occurence of supercells, modulated structures, and/or disordred intregrowths.

The possibility to tune in a controlled way various pristine frameworks opens a wide field of investigation for tailor-made crystallographic architectures. This fascinating crystal chemistry upon oxidation and reduction will be described and rationalized for a global vision of these giant anion/cation-labile systems.

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Keywords: metal exsolution, topochemical transformation, metal depleted lattices



Complex structures of minerals at Deep Earth conditions: experiments and perspectives

Marco Merlini1

1. Department of Earth Sciences, University of Milano, Milano, Italy

email: marco.merlini@unimi.it

The development in the last decades of high-pressure/ high-temperature devices for synthesis and in-situ analysis, allowed the determination of complex structures of minerals stabilized at deep Earth conditions. Furthermore, the discovery in these experiments of unpredicted stoichiometry in Earth's mantle minerals indicate the possible existence of a number of crystalline phases in the planetary interiors unconceivable before. Multiphase and single-phase experiments, combined with conventional and advanced analytical approaches (i.e. X- ray laboratory, X-ray synchrotron and electron single crystal diffraction) are the basis for building an improved mineralogical model for the Earth's interior. Recent results are provided. The first example shows the possible complexity of hydrous mineral phases in subduction environment, where crustal minerals are transferred in the deep Earth, with implication for water storage and transfer in the Earth's interior and consequent large-scale geological processes. The second example about carbonate structures at extreme conditions indicates a complex crystal chemistry with important geochemical implications in the lower mantle. The third example related to iron-oxides reveal a number of unknown stoichiometry in the planetary interiors, with consequence in the global oxidation states of planets. Most of these structures have no structural analogue in natural and synthetic crystalline materials and can stimulate the design of new functional materials.

Keywords: high-pressure, crystal structure, Earth and planetary interior

KN-10

Hydrides: from Hydrogen Storage to Porous Systems, Structural Design and Solid Electrolytes

Yaroslav Filinchuk¹

1. Universite catholique de Louvain, Louvain-la-Neuve, Belgium

email: yaroslav.filinchuk@uclouvain.be

Hydrogen is traditionally stored in metal hydrides, nowadays seen as too heavy for mobile applications. Complex (ionic solids) and chemical (molecular compounds) hydrides based on light elements, such as N and B, are developed in the recent years, just like porous solids for physisorption of molecular hydrogen. These compounds gave a way to new applications, which I will highlight "in the light of X-rays", as structural studies are often a clue to understanding the functionality.

Firstly, I will show recent attempts to design a molecular system capable to store hydrogen reversibly. Aluminium is the cheap, light and abundant metal used to store hydrogen in a form of alane AlH₃ and alanates AlH₄^{-.} We have developed systems based on Al with complex and chemical hydrides coordinated to it, such as ammonia borane NH₃BH₃ (AB), amidoborane NH₂BH₃⁻ and borohydrides BH₄ [1]. We showed [2] that the ability of the strong Lewis acid Al³⁺ to coordinate both the initial hydrogenated species as well as their dehydrogenation products makes it a good template for chemical transformations of hydrides. In particular, AB coordinated to Al³⁺ in Al(BH₄)₃·NH₃BH₃ endothermically dehydrogenates to a single product identified as Al(BH₄)₃·N-HBH, with a potential for a direct rehydrogenation of AB.

Secondly, porous materials can be also made of hydrides [3]. We investigated gas sorption in the porous γ -Mg(BH₄)₂ using neutron powder diffraction to accurately localize the guests and synchrotron X-ray powder diffraction to collect data along the adsorption isobars. The latter allows to study structural changes with pressure and temperature variation, giving insight into guest-host and guest-guest interactions, as well as to extract relevant thermodynamic parameters. I will discuss the intermolecular interactions, size effects and the role of hydridic hydrogen in physisorption. In this small pore system, the effect of the probe size on the loading capacity and the location of the guest molecules is remarkable. While typically each pore can be occupied by one or two larger guests, the amount of hydrogen can go up to 5 molecules per pore, yielding the total capacity of 2.33 H₂ molecules per Mg atom. We are trying to extend the family of hydridic porous solids by combining imidazolates (ligands known to build stable frameworks) and complex hydrides (should be responsible for the unusual functionality). The approach and recent results will be presented.

Thirdly, complex hydrides are known as good solid state electrolytes that may eventually allow to build safe all-solid-state batteries.

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KN-11

Vagando entre los picos - ¿cómo llegué hasta aquí? Improving methods in data collection and processing

Harry Powell1

1. Harry Powell Crystallographic, London, United Kingdom

email: hrp1000@virginmedia.com

Both data collection and data processing methods have changed dramatically during the history of X-ray crystallography, but the pioneers in the field would still recognise much of what we do today. Developments in electronics (which barely existed when von Laue and the Braggs made their first steps towards structure solution, e.g. [1]) have given rise to huge advances in detector hardware and computational methods, but we still measure the position and intensities of diffraction maxima and use this information to determine structural properties of materials - albeit at a rate that might astonish our forebears.

In a discussion of various moving-crystal and moving-detector methods of data collection, I will discuss how modern data processing has allowed single crystal data collection methods to converge on a moving-crystal-static-detector method that was formalised in the late 1970s [2], just as I left school. I will discuss some of the important milestones together with a view of some of the more interesting side-roads that have been explored over the decades. As I wander amongst the (diffraction) peaks, I will try to answer the question "how did we get here?".

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Keywords: data collection, data processing, historical

KN-12

Free-standing nanostructures at atomic scale: from growth mechanisms to local properties

Jordi Arbiol1

 Advacned Electron Nanoscopy, ICREA and Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Bellaterra, Barcelona, Spain

email: arbiol@icrea.cat

Technology at the nanoscale has become one of the main challenges in science as new physical effects appear and can be modulated at will. Semiconductor materials for electronics, optoelectronics, sensing and energy applications are taking advantage of the low dimensionality, improving their properties and opening a new range of applications. As developments in materials science are pushing to the size limits of physics and chemistry, there is a critical need for understanding the origin of these unique physical properties (optical and electronic) and relate them to the changes originated at the atomic scale, e.g.: linked to structural changes of the material, many times related to the presence of crystal defects.

In the present work, I will show how combining advanced electron microscopy imaging with electron spectroscopy, in an aberration corrected STEM will allow us to probe the elemental composition and electronic structure simultaneously in unprecedented spatial detail.

The talk will focus on several examples in advanced semiconductor nanomaterials for optical, electronic and energy applications. In this way the latest results obtained by my group on direct visualizing and modeling materials at atomic scale will help to understand their growth mechanisms (e.g.: how the occurrence of a single twin defect can modify the growth from 1D (nanowire) to 2D (nanosheet) [1,2]) and also correlate their physical properties (electronic and photonic) at sub-nanometer with their atomic scale crystal structure. The examples will cover a wide range of semiconductor nanomaterials: quantum structures self-assembled in a nanowire: quantum wires (1D) [3] and quantum dots (0D) [4,5] and other complex nanowire-like morphologies for photonic and energy applications (LEDs, lasers, quantum computing, single photon emitters, water splitting cells, batteries) [7,8,9,10], as well as nanomembranes and 2D sheets [8,11].

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Keywords: Transmission electron microscopy, nanomaterials, structure

KN-13

Taking on the next structural challenges posed by polycrystalline materials

Lynne McCusker¹, Christian Baerlocher¹

1, ETH Zurich, Zurich, Switzerland

email: mccusker@mat.ethz.ch

Three decades ago, the determination of the crystal structure of a polycrystalline material using X-ray powder diffraction (XPD) data was a challenge, requiring a dedicated and patient crystallographer. Today, the necessary tools have been developed, and such analyses are conducted worldwide in all areas of science on a routine basis. During this time, we have also watched the definition of a single crystal change. The 100mm crystal previously required for data collection in a laboratory using a point detector could be reduced to 30mm with an area detector, and to just a few mm with synchrotron microdiffraction techniques. More recently electron diffraction and X-ray Free Electron Lasers have reduced this requirement still further into the nanometer range. Does this mean that the job is done and we should seek other challenges?

Like all areas of science, it is always possible to dig deeper. It can be argued that developing methodology and instrumentation to address the initial phase problem was just the first step in the elucidation of the structure of a polycrystalline material. The structural details that become evident during the course of a Rietveld refinement continue to pose new challenges. Probably the most common of these is the presence of some element of disorder. Even with single-crystal data, the full analysis of the diffuse scattering that accompanies any disordered structure still lies within the realm of the experts, but with a little persistence some useful information can be extracted from the Bragg peaks alone. How far can we go with XPD data? For example, can the disordered organic structure-directing agents used in zeolite syntheses be located in the final product using XPD data? Yes, they can.

Can other techniques help us overcome some of the limitations inherent to XPD data? In our own research we have come to appreciate the complementarity of XPD, electron microscopy/diffraction and solid state NMR techniques. For example, the conformer disorder in D-ribose was first indicated by MAS NMR, the framework disorder in the niobium silicate AM-11 could be seen in electron microscopy images, and the unexpected structure of the inner surface of the disordered zeolite catalyst SSZ-70 could only be fully characterized via sophisticated NMR techniques. Combining techniques requires manual intervention and tenacity, but the results are worth the effort. A few examples of such studies will be presented.References:

Keywords: powder diffraction, disorder, zeolites

KN-14

New insights into making and breaking crystals

Aurora Cruz-Cabeza1

1. School of Chemical Engineering and Analytical Sciences, The University of Manchester, Manchester, United Kingdom

email: aurora.cruzcabeza@manchester.ac.uk

At the crystallisation group at Manchester, we have had a long-standing interest in the study of crystal nucleation and growth (making crystals). Understanding, designing and controlling robust crystallisation processes is key for the production of crystalline materials. More recently, we have also developed an interest in understanding the processes of milling (breaking) crystals. How crystals break, the structures afforded and their kinetics, are fundamental concepts that need to be understood in order to apply milling techniques during the formulation of tablets. This keynote lecture reviews some recent advances in the understanding of nucleation and milling processes in small molecule crystals.

First, I present our recent work in the study of the kinetics of nucleation of a series of four aromatic carboxylic acids in different solvents and at different supersaturations [1]. After computing a myriad of parameters, we found some revealing correlations between nucleation rates and the strength of the aromatic stacking involved in the growth of the crystals under study. This revealed, that the weakest continuous interaction, was controlling the kinetics of crystal nucleation at the molecular level.

Second, we study the kinetics of the conversion of theophylline into a solvate by milling. Theophylline converts into a 1:1 solvate and then into a 1:1.5 solvate with pyrrolidone upon grinding in increasing amounts of pyrrolidone. Whilst the kinetics of the conversion to the 1:1 solvate were very fast, formation of the 1:1.5 solvate was slow. We found that the kinetics of breaking the reactant crystals were controlling the kinetics of the overall process [2].

Third, we study a molecular system which can exist in two different polymorphs (A and B). Polymorph A can only be obtained by dry milling or milling in the presence of small amounts of solvent. Our investigations showed that our milling experiments always lead to the thermodynamically stable form. However, the thermodynamically stable form switches from B to A as the size of the crystallites becomes smaller [3].:

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Chemical Science, 2016, 7, 6617.

Keywords: nucleation, milling, polymorphism

KN-15

Porous Crystalline Architectures: Ultrafast Molecular Rotors and Dynamics Control by Gas Stimuli

Angiolina Comotti¹, Fabio Castiglioni¹, Silvia Bracco¹, Alessandro Pedrini¹, Jacopo Perego¹

1. Department of Materials Science, Milan, Italy

email: angiolina.comotti@unimib.it

A challenging issue is the dynamics of nanoporous solids after the insertion of molecular rotors in their building blocks, promising access to the control of rotary motion by chemical and physical stimuli.[1] The combination of porosity with ultra-fast rotor dynamics was discovered in molecular crystals, covalent organic frameworks and MOFs by ²H spin-echo NMR spectroscopy and T1 relaxation times.[2-5] The rotors, as fast as 1011 Hz at 150 K, are exposed to the crystalline channels, which absorb CO₂ and I₂ from the gas phase, even at low pressures. Interestingly, the rotor dynamics can be switched on and off by vapor absorption/desorption, showing a remarkable change of material dynamics, which, in turn, produces a modulated physical response. Novel mesoporous organosiloxane frameworks allowed us to realize periodic architectures of fast molecular rotors on which C-F dipoles are mounted.[6] These dipolar rotors showed not only rapid dynamics (109 Hz at 325 K) in the solid-state NMR experiments, but also a dielectric response typical of a fast dipole reorientation. Moreover, crystals with permanent porosity were exploited in an unusual way to decorate crystal surfaces with regular arrays of dipolar rotors. The inserted molecules carry alkyl chains which are included as guests into the channel-ends. [7] The rotors stay at the surface due to a bulky molecular stopper which prevents the rotors from entering the channels. The host-guest relationships were established by 2D solid-state NMR and GIAO HF ab initio calculations. In a final example, flexible molecular crystals were fabricated by a series of shape-persistent azobenzene tetramers that form porous molecular crystals in their trans configuration. The efficient trans-cis photoisomerization of the azobenzene units converts the crystals into a non-porous phase but crystallinity and porosity are restored upon $Z \rightarrow E$ isomerization promoted by visible light irradiation or heating. We demonstrated that the photoisomerization enables reversible on/off switching of optical properties as well as the capture of CO₂ from the gas phase.[8] We would like to thank Cariplo Foundation, Lombardy Region/INSTM Consortium and MIUR (PRIN 2016).

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Keywords: porous crystals, molecular rotors, gas sorption

KN-16

Transforming co-crystals from form to function: Fact, fancy, and great expectations

Christer Aakeroy1

1. Department of Chemistry, Kansas State University, Manhattan, KS, United States of America

email: aakeroy@ksu.edu

The precise orientation and organization of molecules in a crystalline lattice determine many bulk properties of the substance, *e.g.* density, solubility, thermal stability, hygroscopicity, and mechanical strength. Consequently, if we are seeking to fine-tune or 'dial-in' physical properties through a bottom-up approach, then we need to acquire control over the metrics and topologies of the structural landscape that is inhabited by a particular target molecule. Unfortunately, this presents considerable challenges because all molecular recognition events are the result of a delicate balancing act between relatively weak and reversible non-covalent interactions.

One of the reasons why co-crystals may offer unique opportunities for deliberate adjustments of bulk properties is that within a series of co-crystals of a target molecule, it may be possible to make modular changes to the crystalline framework that contains the "active" molecules. This, in turn, may allow us to make incremental changes to physical properties of a substance without having to alter the molecular properties of the target. The inexorable (but not always obvious) connections between structure and properties means that with the ability to change specific aspects of the solid form of a compound comes new and unique prospects for materials design.

This presentation will describe different strategies for the design and practical synthesis of co-crystals using both hydrogen- and halogen bonds, and will also offer several examples of co-crystal technology as applied to both energetic materials and agrochemicals.

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Keywords: Co-crystals, intermolecular interactions, materials

MS01 - Micro & nano crystals in MX

Chairs: Dr. Helen Ginn, Dr. Thomas White

MS01-01

VMXm: A new micro/nanofocus protein crystallography beamline at Diamond

Anna Warren¹, Gwyndaf Evans¹, Jose Trincao¹, Emma Beale¹, Adam Crawshaw¹, Graham Duller¹, Andy Stallwood¹, Mark Lunnon¹, Dave Butler¹

1. Life Science, Diamond Light Source, Didcot, United Kingdom

email: anna.warren@diamond.ac.uk

VMXm is a new micro/nanofocus protein crystallography beamline currently being constructed at Diamond Light Source. The beamline is designed to measure multiple rotation data sets from microcrystals down to 0.5 microns in size and minimise the sample material required for structure determination. The beamline optics will deliver a beamsize of 0.3 - 10 µm vertically, using a single custom profiled fixed focal length mirror, and 0.5 - 5 µm horizontally via a two stage demagnification scheme and a variable secondary source aperture. The beamline will operate at energies between 6 and 28 keV delivering between 1011 and 1012ph/s to the sample (at 12 keV), depending on the optical configuration. Crystal samples will be visualised and aligned to the X-ray beam using a built-in Scanning Electron Microscope (SEM). Samples will be prepared on TEM grids, using plunge freezing techniques taken from cryo-EM. To further improve signal to noise, data will be collected from samples under vacuum. The design of the beamline will be presented, along with sample preparation techniques for submicron crystals and initial data collection results from the beamline

Keywords: Instrumentation, microcrystallography, protein crystallography

MS01-O2

Applications for serial crystallography at synchrotrons

Tobias Weiner¹, Daniel James¹, Przemysław Nogly², Meitian Wang³, Jörg Standfuss¹

- 1. Laboratory of Biomolecular Research, Paul Scherrer Institut, Villigen, Switzerland
- 2. Department of Biology, ETH Zürich, Villigen, Switzerland
- 3. Photon Science, Paul Scherrer Institut, Villigen, Switzerland

email: tobias.weinert@psi.ch

Serial millisecond crystallography (SMX) at synchrotrons allows typical crystallographic experiments to be performed at room-temperature. High-resolution structure determination and even native SAD phasing from small crystals becomes possible when using modern high frame-rate detectors¹. Using a continuous room-temperature setup opens the door to new types of experiments.

Time resolved serial femtosecond crystallography at free electron lasers (FELs) can be performed with the same high viscosity injectors² that are used for SMX at synchrotrons³. The synergy between synchrotrons and FELs allows for more efficient use of precious beamtime at FELs, demonstrated in our recent LCLS beamtime in which we recorded over a million diffraction patterns of Bacteriorhodopsin.

The high frame rates of modern detectors offer a convenient way towards time resolved experiments without special beamline equipment, which may help bringing time resolved crystallography out of its niche.

Keywords: room-temperature, time-resolved, serial crystallography

MS01-O3

Serial protein crystallography in living insect cells

J. Mia Rudolph¹, Robert Schönherr², Lars Redecke³

- 1. University of Lübeck, Biochemistry & CFEL, DESY, Hamburg, Germany
- 2. DESY, Photon Science, Hamburg, Germany
- 3. University of Lübeck, Biochemistry & DESY, Lübeck, Germany

email: rudolph@biochem.uni-luebeck.de

Protein crystals in living cells have been observed in all domains of life [1]. This crystallization approach holds the possibility to grow a huge number of micron-sized protein crystals with comparable properties and of high quality in a short time [2-3]. In order to systematically exploit the potential of *in cellulo* crystallization in living insect cells for structural biology, we are establishing a streamlined process to rapidly elucidate the structural information of *in cellulo* crystallized target proteins.

After cloning the gene of interest into baculovirus transfer vectors, the associated recombinant baculoviruses are generated to infect insect cells. Crystal formation is detected at day 3 to 5 after infection. If intracellular crystallization was successful, diffraction data of the isolated in cellulo crystals are collected using serial crystallography approaches either at XFELs or highly brilliant synchrotron sources, depending on the crystal diffraction volume. The thousands of generated diffraction patterns are processed either with CrystFEL or XDS. In our hands, these efforts resulted in the successful crystallization of more than 20 different proteins in living insect cells so far. However, a broader application is currently restricted by two major bottlenecks: Firstly, depending on the recombinant protein, the fraction of crystal containing cells varies between more than 80 % and less than 1 %. And secondly, changes of environmental conditions during cell lysis and crystal purification result in a loss of crystal quality.

To overcome these limitations we recently established techniques for serial diffraction data collection from in cellulo grown crystals directly within living insect cells, using synchrotron and XFEL radiation both at RT and cryo conditions. These innovative approaches avoid crystal purification and transfer of the living, crystal-containing cells, and furthermore allow direct screening of cell cultures for successful in cellulo protein crystallization using the X-ray beam. Ultimately, our current in cellulo crystallization pipeline will be further improved to overcome limitations in data collection due to low intracellular crystallization efficiency, supported by an additional integration of fluorescence-based cell sorting, enriching the proportion of crystal containing cells. Our results pave the way to a more efficient use of crystal containing insect cells as suitable targets for serial diffraction data collection at synchrotrons and XFELs in the future

Keywords: serial crystallography, in cellulo, SFX

MS01-O4

Nanobeam precession-assisted 3D electron diffraction reveals a new lysozyme polymorph

Arianna Lanza¹, Valentina Cappello¹, Eleonora Margheritis¹, Enrico Mugnaioli¹, Mauro Gemmi¹, Gianpiero Garau¹

 Center for Nanotechnology Innovation, Istituto Italiano di Tecnologia, Pisa, Italy

email: arianna.lanza@iit.it

Besides the well-established X-ray diffraction, the structural investigation of biological macromolecules can rely on new recently developed techniques. Among these, serial crystallography at X-FELs, single particle cryo-electron microscopy and electron diffraction (ED) allow overcoming the challenges posed by large biomolecules, namely (i) the necessity of preserving hydration, (ii) the difficulty to grow large and well-ordered crystals and (iii) the challenge posed by their high beam sensitivity. ED is particularly promising, because electron microscopes are much more readily available than X-FELs and diffraction methods normally allow higher resolution than imaging methods. Nevertheless, applications of 3D ED to structural biology had not been pursued until very recently, when the feasibility was demonstrated on 3D (sub)micro crystals of test-case protein samples.[1,2]

So far, plunge-frozen macromolecular crystals have been investigated in selected area electron diffraction (SAED) mode while the sample was continuously rotated in order to speed the acquisition time and collect a comprehensive data set before the crystal deteriorates due to beam damage. In this contribution we present the first application of nanobeam precession-assisted 3D ED to biological macromolecules. The advantages of this approach with respect to typical SAED methods employed so far are: (i) the reduction of illuminated sample area, (ii) the possibility to track crystal position during sample tilt and (iii) the chance to get multiple data sets from the same crystal.[3]

Our ED data collection strategy has been successfully applied on the well-known hen egg white lysozyme (HEWL), and allowed us to identify a new monoclinic polymorph that crystallizes only in form of micrometric acicular crystals. The crystal structure of this HEWL polymorph could be solved by molecular replacement, making it the first unknown complete protein crystal structure ever solved by ED.

Keywords: Electron diffraction, proteins, nanocrystals

MS01-05

Serial micro- and nano-crystallography at the European XFEL: Capabilities of and first results from the SPB/SFX instrument

Stephan Stern¹

1. European XFEL, Hamburg, Germany

email: stephan.stern@xfel.eu

The rapid evolution of micro- and nanocrystallography as an important and distinct field of macromolecular crystallography was, from its very beginning, closely tied to the advent of ultrafast, pulsed x-ray sources of the 4th generation such as X-ray free-electron lasers (XFELs). Today, serial femtosecond nanocrystallography experiments at XFELs have proven to be a powerful method for time resolved studies of fundamental biological dynamics on the molecular level, ranging from enzyme-substrate mixing to photo-induced timed resolved dynamical processes. For the new X-ray free-electron laser facility European XFEL, dynamical biology in the sense of time resolved micro- and nanocrystallography was determined to be one of the major pillars of scientific research, and the envisaged X-ray pulse repetition rates in the Megahertz regime at European XFEL promise to offer unique capabilities for data collection for such experiments.

Here, we present capabilities, experiences and results from the first run of experiments at the SPB/SFX scientific instrument of the European XFEL. We give an overview of the general design and capabilities of the instrument and outline what benefits and challenges come from the uniquely high X-ray repetition rate. This includes the consequences for sample delivery, detector calibration, data collection and experimental performance in general. We further outline the capabilities for ultrafast time resolved studies at SPB/SFX aided by an optical laser system that follows the European XFEL's MHz pulse structure. Finally, plans for the incorporation and commissioning of new X-ray focussing mirror optics, and the installation of two additional experimental interaction regions at SPB/SFX will be presented and are envisaged to greatly enhance the experimental capabilities of the instrument for micro- and nanocrystallography.References:

Keywords: XFEL, instrument, time-resolved

MS02 - From data collection to structure finalization: getting the most from your crystal

Chairs: Dr. William Shepard, Dr. Katherine McAuley

MS02-O1

Achieving higher performance in highthroughput compound and fragment screening campaigns by using "Club Class" data collection, Pipedream and CRIMS

Gerard Bricogne¹, Gerard Bricogne¹, Claus Flensburg¹, Peter Keller¹, Wlodek Paciorek¹, Andrew Sharff¹, Clemens Vonrhein¹, Jose Antonio Marquez², Djordje Musil³

1. Global Phasing Ltd., Cambridge, United Kingdom

- 2. HTX Laboratory, EMBL Grenoble Outstation, Grenoble, France)
- 3. Discovery Technologies, Merck KGaA, Darmstadt, Germany)

email: gb10@globalphasing.com

Fourth-generation X-ray sources, fast sample delivery systems for micro-crystals and pixel-array detectors with ever faster frame rates are radically extending ways of collecting diffraction data, while associated software developments are creating a continuum of options between serial experiments at synchrotrons and at XFELs.

From the viewpoint of structure-based drug discovery, these developments will give better access to targets for which "macro-crystals" cannot be obtained, but they will do so at a greatly increased cost. This encourages renewed efforts to more fully exploit the intrinsic advantages of macro-crystals, when available, through better experiments. Unfortunately, strong emphasis on automation and speed in typical high-throughput data collection workflows has left little room for invoking any form of expert decision making in data collection without considerable disruption of automation.

An unlikely opportunity linked to the development of the Diamond I23 experimental phasing beamline (Armin Wagner) has enabled us to address this limitation via a "Third-party design and control" approach that makes our solution transferable between different beamline software environments with minimum effort. This approach has been validated by the live execution of our workflows on Diamond beamlines running under the GDA control software, and recently on the ESRF ID30B beamline running under MXCuBE.

We have been able to demonstrate that "Club Class" multi-orientation datasets can significantly enhance the detection and characterisation of small weakly bound fragments - a process fundamental to fragment-based drug discovery - in the context of a fragment screening campaign. Numerous datasets collected on the ESRF MASSIF-1 beamline were processed with the Global Phasing "Pipedream" software suite that seamlessly combines automated data reduction and model refinement with ligand density elicitation, automated ligand fitting and ligand geometry validation. New interfaces for the ranking and evaluation of Pipedream results were developed within the Crystallization Information Management System (CRIMS) in order to support rapid analysis and decision making in the context of large-scale compound and fragment screening campaigns. The use of a small number of "Club Class" datasets (manually collected on the ESRF ID30B and SLS PX-III beamlines) led to a significant increase in the number of hits and enabled a complete elucidation of initially ambiguous binding modes for a number of challenging fragments. The approach described here is widely applicable and illustrates the potential of the combined use of "Club Class" data collection strategies and of fully automated protein-to-structure X-ray crystallography pipelines to achieve higher performance in large-scale compound and fragment screening campaigns.

Keywords: Fragment screening, multi-axis goniometry, ligand detection sensitivity

MS02-O2

The ultimate experiment

Ana Gonzalez¹

1. MAX IV, Lund, Sweden

email: ana.gonzalez@maxiv.lu.se

Data collection is often described as the last experimental step in crystallographic experiments. The reason is that the choice of data collection parameters and strategy will influence the quality of the data which in turn will determine the amount of information that subsequent data processing and phasing software can be extract from the data, the quality of electron density maps and, ultimately, the failure or success of the experiment.

Unfortunately there is not a simple one-fits-all recipe to collect good data. The optimal strategy depends on the experimental purpose, the characteristics of the X-ray beam and instrumentation used to collect data and the samples properties. Radiation damage is often a critical factor limiting data quality and being able to predict the absorbed dose and mitigate the effects of exposure to X-rays is very important to a successful experiment.

While some general principles and guidelines to obtain good data are often successfully followed, blind application of rules of thumb can sometimes result in suboptimal experiments due to the conflicting effects of different data collection practices. Strategy programs developed over the last decade are in use at many dedicated macromolecular crystallography beamlines provide good guidance; however human experience is still beneficial to interpret software output and make the best decicions in difficult cases. Understanding the role of all the different factors on data quality is key to designing a reasonable data collection strategy that offers the best compromise between conflicting requirements and facilitates data processing and structure solution.

Keywords: Data collection, experimental strategy, radiation damage

MS02-O3

ARCIMBOLDO_SHREDDER: making the most of good data despite having only a poor homolog

Claudia Lucía Millán Nebol¹, Massimo Domenico Sammito¹, Airlie J. McCoy², Robert D. Oeffner², Teresa Domínguez-Gil³, Juan A. Hermoso³, Randy J. Read², Isabel Usón¹

- Structural Biology Unit 'Maria de Maeztu Unit of Excellence' - Institut de Biologia Molecular de Barcelona (IBMB-CSIC), Barcelona, Spain
- 2. Cambridge Institute for Medical Research, University of Cambridge, Cambridge, United Kingdom
- Department of Crystallography and Structural Biology, Instituto Química Física 'Rocasolano' CSIC, Madrid, Spain

email: cmncri@ibmb.csic.es

Good native data are an asset for phasing, because they allow you to obtain and improve solutions to the phase problem even in the absence of a suitable homologous template. The question often explored in Molecular Replacement (MR) is: Is the model good enough to solve the structure? Here we explore the reverse: Are the data good enough for the distant homolog model to succeed? ARCIMBOL-DO_SHREDDER (1) derives compact model fragments starting from a distant homolog template, evaluating their performance in a process driven by the experimental data, provided that a resolution of at least 2.5 Å is available. This method uses partial fragments that need to be very accurate. The following stages can be distinguished:

- Partition and annotation of the template: The template model is dissected into fragments that will be disassembled to give the model additional degrees of freedom.
- Generation of the models: The size of the fragments is derived from a target eLLG, set to be large enough to find correct solutions, but small enough to generate potentially accurate fragments.
- Evaluation against the likelihood rotation-function target
- Gyre refinement (2): The orientation and relative translation of the rigid groups identified in the first step are refined against the rotation-function target.
- Translation search
- Packing test
- Refinement: Depending on the data and the expected deviation of the models, a set of different strategies can be trialed at this stage: refinement of the r.m.s. error attributed to the model, superposition of the original template on each placed fragment with trimming and refinement, *gimble* refinement against the likelihood translation-function target subdividing the model into the same rigid groups as in gyre, or phaser's likelihood-based pruning.
- *Phase combination*: Consistent phase sets can be combined with *ALIXE* in order to complete partial solutions and increase their information content.

 Density modification and autotracing for expansion of the substructure to a full solution: The single or combined phase sets are used to calculate starting maps for iterative density modification and autotracing with SHELXE.

The method described has been successful in solving previously unknown structures, including Slt (3), a lytic transglycosylase from the pathogen *Pseudomonas aeruginosa*. Moreover, it has helped to increase our knowledge about how to best exploit the available data and models in the context of fragment-based MR. In this presentation, both the method and its application to different cases will be discussed.

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 Proceedings of the National Academy of Sciences DOI: 10.1073/ pnas.1801298115

Keywords: molecular replacement, small fragments, distant homologs

MS02-O4

Ctrl-D, a versatile tool for analyzing processed diffraction data

Fabio Dall'Antonia1, Gleb Bourenkov1, Thomas Schneider1

1. European Molecular Biology Laboratory, Hamburg Unit, Hamburg, Germany

email: fabio.dallantonia@embl-hamburg.de

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- *Partition and annotation of the template:* The template model is dissected into fragments that will be disassembled to give the model additional degrees of freedom.
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Keywords: Data-analysis, SSX, SAD-Phasing

MS02-O5

Optimized diffraction data collection for native SAD phasing

Naohiro Matsugaki¹, Yusuke Yamada¹, Masahiko Hiraki¹, Ayaka Harada², Miki Senda², Toshiya Senda²,

1. Photon Facroty, Structural Biology Research Center, Tsukuba, Japan

2. Structural Biology Research Center, Tsukuba, Japan

email: naohiro.matsugaki@kek.jp

Phasing macromolecular crystals by native SAD (single-wavelength anomalous dispersion) is attractive for de-novo structure determination because no derivative crystals are required. However, the method has been uncommon for 30 years due to experimental difficulties in using long wavelength X-ray required to enhance weak anomalous signals from naturally-presented light atoms in macromolecules. In diffraction measurement, long wavelength X-ray beam is severely absorbed by the sample or by the air on the beam path, which deteriorates the quality of diffraction data and results in burying small anomalous differences.

Diffraction data collection environment for native SAD phasing should be considered taking the above problem seriously into account. Photon Factory beamline BL-1A is routinely operated for long wavelength experiment where the diffractometer is equipped with a standing chamber enclosing both the goniometer and the X-ray detector, a helium cold stream recycling system, and a specially designed sample changer. X-ray absorption on the beam path does not matter at the beamlin as it is completely covered by helium. Under such optimized experimental environment we showed using the wavelength of 2.7 Å was advantageous in native SAD phasing against 1.9 Å, at around which most native SAD data collection has been performed so far [1].

Another aspect is the absorption by the sample itself. The wavelength used should be optimized for the sample size to most enhance the weak anomalous signal. However anisotropic amount of absorption due to the sample shape would be more problematic, which introuduces systematic errors into the diffraction data. Many trials have been made to correct the absorption effect in both empirical and analytical way, but it's much simpler if the sample is shaped in sphere. Shaping macromolecular crystal with deep UV laser [2] will solve the problem in a routine manner. We will present how the sample shaping is effective in native SAD phasing, as well as the discussion on the relationship between the sample size and the wavelength to be used.

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Keywords: native SAD phasing

MS03 Combining methods in macromolecular structure determination, including special conditions MX

Chairs: Dr. Martin Walsh, Dr. Victor Lamzin

MS03-01

All is fair in phasing: the combined artillery in ARCIMBOLDO

Isabel Usón¹, Claudia Millán Massimo Sammito², Rafael J. Borges², Nicolas Soler², Iracema Caballero², Ana Medina²

1. ICREA at SBU, IBMB-CSIC, Barcelona, Spain

2. SBU, IBMB-CSIC, Barcelona, Spain

email: uson@ibmb.csic.es

Solving the phase problem is often a bottleneck in the determination of macromolecular crystal structures. Our approach to phasing, implemented in the software ARCIMBOLDO (http://chango.ibmb.csic.es/ARCIMBOLDO) relies on the combination of locating partial model fragments such as polyalanine alpha-helices with the program PHASER [1] and iterative density modification and main chain tracing with the program SHELXE [2]. In difficult cases, identifying correctly positioned fragments is not obvious and then many putative groups of fragments have to be tested in parallel. As the starting substructure constitutes a small fraction of the total and needs to be expanded, phasing will be self-validating in most ARCIMBOLDO use cases: once a solution can be identified as correct, it may contain errors but should be fundamentally right. Therefore all available information can be used to constrain the starting hypotheses. Typically used fragments encompass ubiquitous models, such as polyalanine helices, libraries of small local folds such as beta sheets extracted from the PDB and fragments of distant homologs. Restricting the purely ab initio search by predictions derived from bioinformatics can be enhanced with experimental data such as circular dichroism to decide which libraries should be used in ARCIMBOLDO BORGES Alternatively, partial solutions can be filtered with the complementary information to discard incompatible solutions. The placed main chain models can be extended with probable side chains to generate multiple alternatives prior to expansion and we have used mass spectrometry in the context of natural products such as snake venoms, where composition is uncertain, to establish the structure. The combination with experimental phase information, too weak to render a solution on its own, can be performed in a number of ways: anomalous fragments can be searched for in PHASER along with normal fragments or independently determined and referred to the same origin. In either case, they can be combined in SHELXE. Alternatively the anomalous substructure can be determined from the map calculated from the partial fragments. A poor low resolution experimental map may be used in ARCIMBOLDO SHREDDER [3] to phase a higher resolution crystal form.

Keywords: phasing, ARCIMBOLDO, SHELX

MS03-O2

Structural and mechanistic insights into DNA transposition facilitate genetic tool development

Orsolya Barabas¹, Irma Querques¹, Cecilia Zuliani¹, Franka Voigt¹, Lisa Wiedemann², Csaba Miskey², Zoltán Ivics²

- Structural and Computational Biology Unit, European Molecular Biology Laboratory (EMBL), Heidelberg, Germany
- 2. Division of Medical Biotechnology, Paul Ehrlich Institute, Langen, Germany

email: barabas@embl.de

The DNA transposon Sleeping Beauty (SB) is an efficient gene delivery vector with broad utilities in vertebrate genetics and human gene therapy. However, the molecular principles of its transposition remain elusive, greatly hampering rational design of tailored SB variants. In this talk, I will present integrative high-resolution insights into SB transposition and demonstrate how these enable directed engineering of advanced transposon tools. Using a combination of crystallography, SAXS, biochemical, biophysical techniques, molecular modelling and fluorescence cell imaging, we have dissected the assembly pathway of SB's active transposition machinery and showed that it follows a distinct pathway from other known transposons. We visualized the structures of nucleoprotein complexes involved in the onset of transposition, elucidating the basis of the differences between SB and a canonical human element at high resolution. This showed that SB's unique assembly mode critically underlies its exceptional efficiency and allowed us to develop a strategy to chemically control transposition rates in living cells. Guided by our structure of the SB transposase catalytic domain, we further developed custom-made SB variants with increased activity and safety, clearly illustrating the power of structure-guided rational protein design for the advancement of molecular tools.

Keywords: protein-DNA complex, integrating structure and function, genetic engineering

MS03-O3

Observations of ultra-fast light-induced processes in proteins using time-resolved serial femtosecond crystallography

Gabriela Nass Kovacs1

1. Biomolecular Mechanisms, MPI for medical Research, Heidelberg, Germany

email: gabriela.kovacs@mpimf-heidelberg.mpg.de

The ultrashort and highly intense pulses of new X-ray sources, the X-ray Free-electron lasers (XFELs), open the sub-ps time domain for time-resolved crystallography using small crystals that can be efficiently photolyzed. This is particularly appealing for the study of photosensitive proteins, which contain a light-absorbing chromophore that allows exploitation of light energy as a resource or as a carrier of information initiating intra- or intercellular signaling. The ultra-fast light-induced events comprising double-bond isomerization have been the subject of intense research for decades and have been spectroscopically well characterized. However, direct structural information on the excited state and intermediate structures necessary to understand the underlying mechanisms has been inaccessible until recently. We present recent insight on the initial events in photoisomerization obtained by time-resolved serial femtosecond crystallography experiments in combination with time-resolved spectroscopy and quantum chemical calculations. This comprehensive mechanistic insight is not only important for the fundamental understanding of light-driven processes but has practical impact on future developments of fluorescent proteins for optical nanoscopy or retinal proteins for optogenetics.

Keywords: XFELs, time-resolved crystallography

MS03-O4

Solving the phase problem with long wavelength X-ray diffraction

Ramona Duman¹, Armin Wagner¹, Kamel El Omari¹, Vitaliy Mykhaylyk¹

1. Diamond Light Source Ltd, Didcot, United Kingdom

email: ramona.duman@diamond.ac.uk

Harnessing the anomalous signal natively present in proteins, to solve their crystal structures, requires an experimental setup optimised for the tender X-ray regime. Macromolecular crystallography experiments on the long-wavelength beamline I23 at Diamond Light Source, UK, target the absorption edges of anomalously scattering atoms in proteins by collecting diffraction data in a high vacuum environment. This unique experimental setup enables a multitude of phasing opportunities, including Sulphur/Phosphorus single wavelength anomalous dispersion (S/P-SAD), and also by accessing the absorption edges of metal ions commonly bound by proteins. Examples will be shown of structures solved on the beamline based on the anomalous signal from Sulphur, Iodine, Cadmium, Potassium, Calcium, Gold, Vanadium, among others. It will also be shown how the combination of a vacuum environment and a large curved Pilatus 12M detector yields superior signalto-noise diffraction data, leading to sub-atomic resolution characterisation of certain structural targets.

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Keywords: long-wavelength, MX, S-SAD

MS03-O5

Sample triggering and delivery for timeresolved studies of proteins

Diana Monteiro Henning Tidow¹, Arwen Pearson¹, Martin Trebbin¹

1. CUI, University of Hamburg, Hamburg, Germany

email: diana.monteiro@uni-hamburg.de

Dynamically resolved, or better known time-resolved, structural studies of proteins rely on specific sample environments at both synchrotrons and XFELs due to two main requirements: the continuous delivery of fresh sample to the X-ray beam and the need to trigger the protein activity. The two most widely used methods for protein triggering are the diffusion of actuators by rapid mixing and light activation using laser pulses. Within collaborative efforts between the Trebbin group and other groups at the University of Hamburg, DESY and ESRF, we have developed sample environments and methods for these complex studies. Specifically, we have recently performed a light-triggered solution scattering experiment employing photocaging to follow a protein dimerisation event at the white-beam station ID09 (ESRF). We have also developed different X-ray compatible devices for serial synchrotron crystallography (SSX) data collection in flow with mixing for which I will present an example using 3D-printed microfluidic devices at beam line ID303-A (ESRF). These versatile methods can be tailored to the requirements of the protein target characteristics such as time scales of reaction and sample form (solution or microcrystalline slurry). Therefore, the developing general and user-friendly sample environments is an important step in making these experiments more widely available.

Keywords: time-resolved, microfluidics, photocaging

MS04 Biophysical characterization and crystallization

Chairs: Dr. Andrzej M. Brzozowski, Dr. Pavlina Rezacova

MS04-01

Biophysical methods for analyzing protein quality

Annette Roos1, Yasmin Andersson2

- Biophysical Screening and Characterization Facility, Drug Discovery and Development Platform, SciLifeLab, Uppsala, Sweden
- Protein Expression and Characterization Facility, Drug Discovery and Development Platform, SciLifeLab, Stockholm, Sweden

email: annette.roos@icm.uu.se

Science for Life Laboratory (SciLifeLab) is a Swedish national center for molecular biosciences supported by the Swedish government. The aim is to make state-of-the-art technologies and know-how available to academic researchers across the whole of Sweden. The Drug Discovery and Development (DDD) Platform is one part of the center. We help Swedish academic groups progress therapeutic ideas towards a pre-clinical proof-of-concept. Projects can have a small molecule focus or the aim can be to produce an antibody therapeutic. The platform consists of eight facilities with different areas of expertise, including assay development and high-throughput compound screening, antibody generation, protein expression, biophysical characterization, medicinal chemistry, pharmacological profiling, analysis of drug metabolism and pharmacokinetics data, and target safety analysis. For more information see https://www. scilifelab.se/platforms/ddd

At the Biophysical Screening and Characterization Facility in the DDD Platform, we characterize interactions between molecules. Our three key techniques are surface plasmon resonance (SPR), X-ray crystallography, and microscale thermophoresis (MST). Most of our DDD projects are to verify binding of compounds found through high-throughput screens. Our objective is to improve the high-throughput hits to become lead molecules.

A recurring problem within many of the projects has been the lack of a functioning reference compound to verify that the target protein behaves in an expected manner. The quality of protein samples is critical in all the techniques we offer, but the lack of reference compounds makes it even more important. The proteins we work with are either provided by the academic group we collaborate with, are bought from companies that provide such services, or are produced by our sister facility within the DDD, the Protein Expression and Characterization Facility. At the DDD we prefer the latter as here we know the protein samples will be well characterized and we can have a dialogue about producing protein in a manner suited to the needs of the project. The analysis methods we mainly use are size exclusion chromatography, various gel electrophoresis, differential scanning fluorimetry (also known as thermal shift assays) and dynamic light scattering.

This talk will discuss some of the older as well as newer methods for characterizing a protein sample prior to crystallization or running a binding assay. The talk will have an educational tone with the hope of stirring up discussions around protein quality and how best to assess it.

Keywords: protein analysis, biophysical methods

MS04-O2

Towards a better understanding of the nucleation process and advanced detection of nanocrystals

Christian Betzel^{1,3}, Robin Schubert¹, Qing-di Cheng¹, Hsiang-Yu Chung², Shih-Hsuan Chia², Guoqing Chang², Franz X. Kärtner^{2,3}, Markus Perbandt^{1,3}, Christian Betzel^{1,3}

- 1. Laboratory for Structural Biology of Infection and Inflammation, c/o DESY, Build. 22a, Notkestrasse 85, 22607 Hamburg, Germany
- 2. Center for Free Electron Laser Science, Notkestrasse 85, 22607 Hamburg, Germany
- 3. Hamburg Center for Ultrafast Imaging, Hamburg, Germany

email: christian.betzel@uni-hamburg.de

At synchrotron (SR) and Free-Electron-Laser (FEL) beamlines micro-sized crystals are preferred for diffraction data collection. Therefore, advanced and reliable methods to prepare and score 3D micro- and nano-crystal suspensions need to be established in time. A better understanding of the nucleation process is of fundamental importance in this context. Till now the nucleation process is discussed in theory and experiment differently. In order to obtain more insights about the process and to obtain supporting evidence for the tow-step nucleation mechanism we investigated the nucleation process and early crystallization events applying complementary biophysical methods [1,2]. In situ dynamic light scattering, small-angle X-ray scattering and transmission electron microscopy experiments were performed. Data obtained strongly support the existence of a two-step mechanism of nucleation. However, the early process is governed by the formation of liquid dense clusters as initial step [3], followed by the transition to higher order assemblies inside these clusters. The desired size for SFX experiments is preferably in the upper nanometer or lower micrometer regime. This guides to a strong demand to develop and establish new methods to analyze, score nanoand micro crystal suspensions for serial crystallography. To support and facilitate this demand we recently designed and constructed a microscope setup based on detecting second harmonic generation (SHG) signals of crystalline particles. This method and setup enhances the already available signal sensitivity to such extend that detection of small crystals and crystals with higher symmetry, known to produce rather weak signals, is now possible and distinguishing between amorphous and crystalline particles is possible as well. The instrument is equipped with additional channels, which are capable to detect the third harmonic generation signal and three-photon excited UV-fluorescence, all in parallel, to provide complementary information about the crystalline sample suspension. Details and experimental data will be presented.

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Keywords: nucleation, crystal-detection, scoring

MS04-O3

The attachment of the lactobacillus surface-layer array to the bacterial cell

Elisabeth Damisch¹, Markus Eder¹, Andela Dordic¹, Krishna Mohan Padmanabha Das¹, Ulla Hynönen², Airi Palva², Janet Vonck³, Monika Oberer¹, Tea Pavkov-Keller⁴

- 1. Institut of Molecular Biosciences, University of Graz, Graz, Austria
- 2. Faculty of Veterinary Medicine, University of Helsinki, Helsinki, Finland
- Structural biology, Max-Planck-Institute of Biophysics, Frankfurt am Main, Germany
- Institute of Molecular Biosciences, University of Graz and ACIB GmbH, Graz, Austria

email: elisabeth.damisch@edu.uni-graz.at

Surface layers (S-layers) are 2D paracrystalline lattices of proteins or glycoproteins which cover the whole cell surface of many Archaea and Bacteria. Since these proteins are in close contact with their habitat they fulfil many vital tasks like bacterial adherence to other cells or substrates, protection against life-threatening conditions and maintenance of the cell shape [1]

S-layer proteins of lactobacilli species have a highly basic pI and are between 25-71 kDa in size [1,2]. They are attached to the cell wall by interaction with lipoteichoic acids (LTA) [1]. It is reported that they are involved in auto- coaggregation and adherence and therefore are significant for the stimulation of gut dendritic cells by interacting with specific receptors [3]. Our goal is to characterize the surface layer proteins SlpA and SlpX of Lactobacillus acidophilus, which are both necessary to build up the protective S-layer coat. By changing the composition of the S-layer coat, the organism is able to adapt to the changing environmental conditions and threats, e.g. osmotic stress. For structure-function characterization, we designed several protein fragments. Soluble fragments were purified and subjected to crystallization. Optimized crystals of the C-terminal fragments, containing the LTA-binding domain, diffracted to 1.8 and 2.2 Å. Crystal structures were solved by SeMet-SAD and the later by molecular replacement. To further characterize the binding of the S-layer to bacterial cell we performed NMR titration experiments and isothermal titration calorimetry measurements with the C-terminal fragment of the protein.

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Keywords: S-layer, Proteins, Lactobacillus acidophilus

MS04-O4

Synthesis and characterization of crosslinked lysozyme crystals filled with singlewalled carbon nanotubes bionanomaterials

Guillermo Escolano¹, Rafael Contreras-Montoya², Juan J. Díaz-Mochón³, Luis Álvarez de Cienfuegos², José A. Gavira⁴

- Departamento de Química Orgánica, Facultad de Ciencias (UGR) and Laboratorio de estudios cristalográficos, Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), Granada, Spain
- Departamento de Química Orgánica, Facultad de Ciencias (UGR), Granada, Spain
- Departamento de Química Farmacéutica y Orgánica, Facultad de Farmacia, (UGR), Centre for Genomics and Oncological Research, Pfizer/UGR/Andalusian Regional Goverment, PTS Granada, Granada, Spain
- Laboratorio de estudios cristalográficos, Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), Granada, Spain

email: gec@ugr.es

Novel bionanomaterials are hybrid materials that include the combination of biomolecules and inorganic substances to generate, enhance or support relevant properties. Bionanomaterials have useful applications in bio- and nanotechnology applications^{1,2}. Among the biomolecules used to prepare hybrid materials, proteins have shown to be versatile materials thank to their capacity to self-assembly in crystalline form generating a porous network of nanometer size. The internal cavities of the protein have the ability to act as template3,4 and it gives the material the possibility to extrapolate nanoscale properties to macroscopic materials for practical applications. In this work, we present a new methodology to homogenously incorporate inorganic particles within protein crystals using dipeptide hydrogels as growth media. To exemplify this methodology, we have obtained lysozyme crystals incorporating single wallet carbon nanotubes at different concentration. Crystals were grown in Fmoc-PhePhe-OH hydrogels5. The influence of the nanotubes on the diffraction properties, hardness, enzymatic activity and conductivity will be presented and discussed, as well as a full characterization of these new materials.

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Keywords: bionanomaterials, crystallization, carbon nanotubes

MS04-O5

Prototyping protein expression constructs with PCR, cell-free expression and fluorescence detection size exclusion chromatography

Martin Bommer1, Udo Heinemann1

1. Max-Delbrueck-Centrum, Berlin, Germany

email: martin.bommer@mdc-berlin.de

Scouting of soluble expression constructs containing a predicted functional domain is time-consuming and appears a gamble. Further, the only direct product is often a size exclusion chromatography trace or the result of a pull-down interaction experiment. The choice of domain boundary, possibly expression tag and host cell grows into a labyrinth of pathways to be navigated by repeated manual cloning, expression and purification trials.

Yet, to allow advances in the most challenging and worthwhile targets, such as integral membrane protein receptors, ingenious methods have been developed to reduce complexity and pre-screen protein production: Cell-free expression [1] circumvents some difficulties encountered during in vivo protein expression and is easily carried out in parallel and at microliter scale. Fluorescence detection size exclusion chromatography (FSEC) [2] of proteins side-steps large-scale cultivation and purification. The green fluorescent protein (GFP)-tagged protein of interest is specifically detected within in a complex mixture.

We sought to combine these methods for the screening of soluble, interaction-competent expression constructs: Candidate gene fragments were amplified and joined to an upstream T7 promoter + solubility tag and a downstream GFP + T7 terminator by overlap-extension PCR (as is used in gene synthesis). The linear PCR products were templates for a commercial cell-free expression kit, which may simply be set up as a hanging drop experiment. Approx. one microliter protein solution was used for each quantification, FSEC or an initial microscale thermophoresis experiment. FSEC traces in the absence or presence of excess unlabelled binding partner provided convincing qualitative results.

We describe a simple setup using off-the-shelf reagents. A wealth of recent literature describes improvements, scale up and add-on experiments.

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Keywords: protein expression, fluorescence, in vitro

MS05 Structural information in drug design

Chairs: Dr. Rob van Montford, Prof. Andreas Heine

MS05-01

X-ray free electron laser: opportunities for drug discovery

Michael Hennig¹, Robert Cheng¹, Rafael Abela¹

1.LeadXpro AG, Villigen, Switzerland

email: michael.hennig@leadxpro.com

Past decades have shown the impact of structural information derived from complexes of drug candidates with their protein targets to facilitate the discovery of safe and effective medicines. Despite recent developments in single particle cryo-electron microscopy, X-ray crystallography has been the main method to derive structural information. Recently, serial crystallography has added new opportunities for X-ray data collection of challenging systems like membrane proteins. Advances in serial crystallography are a pre-requisite to use the unique properties of X-ray Free Electron Laser (XFEL). Unmet peak brilliance and beam focus allow X-ray diffraction data recording and successful structure determination from smaller and weaker diffracting crystals shortening timelines in crystal optimization. To further capitalize on the XFEL advantage, innovations in crystal sample delivery for the X-ray experiment, data collection and processing methods are required. This development was a key contributor to serial crystallography allowing structure determination at room temperature yielding physiologically more relevant structures. Adding the time resolution provided by the femtosecond X-ray pulse will enable monitoring and capturing of dynamic processes of drug molecule binding and associated conformational changes with great impact to the design of candidate drug compounds.

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Keywords: Drug design, X-FEL, serial crystallography

MS05-O2

From fragments to in vivo activity using X-ray crystallography: the discovery of potent inhibitors of the KEAP1-NRF2 protein-protein interaction

Tom Davies1

1. Astex Pharmaceuticals, Cambridge, United Kingdom

email: tom.davies@astx.com

KEAP1 is the key regulator of the NRF2-mediated cvtoprotective response, and an attractive target for diseases involving excessive oxidative stress. Direct antagonism of the KEAP1-NRF2 protein-protein interaction presents a novel opportunity for pharmacological intervention, but identifying inhibitors with drug-like properties has been challenging. In collaboration with GSK, we have applied our fragment-based approach (PyramidÔ) to develop KI-696, a small-molecule KEAP1-NRF2 antagonist which combines high potency with physicochemical properties suitable for biological evaluation. X-ray crystallographic screening led to the identification of fragments bound at multiple "hotspots" within the KEAP1 Kelch domain, and this information was used to elaborate a weakly binding hit (K_d>1 mM) to a potent lead (K_d1.3 nM). KI-696 exhibits good selectivity for KEAP1, and activates the NRF2 antioxidant response in cellular and in vivo models, thereby providing a high quality chemical probe to explore the therapeutic potential of disrupting the KEAP1-NRF2 interaction.

MS05-O3

Effective crystal structures in pharmaceutical development

Sophie Janbon¹

1. AstraZeneca, Pharmaceutical Science, Macclesfield, United Kingdom

email: sophie.janbon@astrazeneca.com

Most crystalline compounds exhibit polymorphism.[1] This is the ability of a chemical substance to pack in different 3-D arrangements. Different polymorphs usually mean different physical and chemical properties. As a result, the pharmaceutical industry invests a significant amount of resources and capabilities in a wide range of polymorph risk-assessment tools [2] to avoid the appearance of a more stable crystalline form of the Active Pharmaceutical Ingredient (API) late in drug development or after launch. One of the main risk of not identifying the most stable form early in drug development is that the business may not guarantee the supply of medicine to patients on time for clinical phases as well as post-launch. Example [3] has existed and showed the criticality of understanding the solid form landscape of any new chemical entity. In the armoury of polymorph risk assessments, the assessment of crystal structure data has become invaluable and this is the main topic of this presentation. This is now a core activity within AstraZeneca, performed on all suitable API's in the portfolio, to 1) guide our experiments, 2) enhance our understanding and 3) risk assess the likelihood of identifying a more stable form. The implementation of the crystal structure assessments has also become an integral part of our form selection process. Following the selection of the solid form for the development and/or commercial phases, crystal structures continue to guide decision-making during the development of commercial processes and control strategies for registered starting materials, chemical intermediates, API's and formulated medicines. Examples of how crystal structures are assessed via a step-wise method, used in our business will be presented using AZ compounds.

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Keywords: Crystal structures, Polymorphs, Risk assessments

MS05-O4

High-Throughput crystallographic fragment screening for drug discovery

Alexander Metz¹, Franziska Huschmann², Johannes Schiebel¹, Uwe Müller², Manfred Weiss², Andreas heine¹, Gerhard Klebe¹

- 1. Institute of Pharmaceutical Chemistry, Philipps-University Marburg, Marburg, Germany
- Helmholtz-Zentrum Berlin, Institute Soft Matter and Functional Materials, Macromolecular Crystallography (HZB-MX), Electron Storage Ring BESSY II, Berlin, Germany

email: alexander.metz@pharmazie.uni-marburg.de

The key idea of fragment screening is that already a small selection of appropriate fragments (-10^3 cpds.) covers a much larger proportion of the overall chemical fragment space (-10^7 cpds.) than a typical high-throughput screening collection ($10^5 - 10^6$ cpds.) with respect to the drug-sized chemical space (-10^{63} cpds.) *dW* < 500 Da). Moreover, in contrast to larger molecules, fragments may bypass strict steric requirements for binding, leading to high hit rates up to 20%. For the same reason fragments often find well-suited anchor positions leading to low-affinity yet highly efficient binding and making them excellent starting points for subsequent ligand design, with the inherent potential to reconstruct the larger lead- or drug-sized chemical space.

Modern semi-automated beamlines are well suited for crystallographic screening of complete fragment libraries or diverse subsets at no higher effort than most pre-screening assays.[1] In conjunction with adequately designed fragment libraries, automated data processing strategies, and optimized crystallographic methodology, this strategy routinely yields large numbers of fragment-bound structures revealing otherwise unanticipated chemotypes and interaction patterns ready to use for structure-based drug design.[2,3]

We present our fragment-screening pipeline at the BESSY synchrotron as well as results from screening the same fragment library against more than 8 diverse proteins. In addition, we present a screen of natural compound-derived fragment structures and results from following up on these with readily available fragment-superstructures suited to fit the remaining parts of the pocket. Finally, we present computational tools to elaborate and evaluate fragment derivatives, e.g. by fragment structure-based docking, also in conjunction with reaction driven de-novo design of easily accessible fragment derivatives.

The presented libraries and methods are part of the Frag2Xtal and Frag4Lead service facility for crystallographic fragment screening soon available at the semi-automated crystallographic BL14.2 at the BESSY II storage ring of the Helmholtz-Zentrum Berlin.

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Keywords: Fragments, Structure-Based Drug Discovery, Computer-Aided Drug Discovery

MS05-O5

Structure-Based design of inhibitors targeting PrfA, the master virulence regulator in *listeria monocytogenes*

Elisabeth Sauer-Eriksson¹, Martina Kulén¹, Marie Lindgren², Christin Grundström¹, Uwe H. Sauer¹, Jörgen Johansson², Fredrik Almqvistⁱ

- 1. Chemistry, Umea, Sweden
- 2. Molecular Biology, Umea, Sweden

email: elisabeth.sauer-eriksson@umu.se

New strategies to combat bacterial infections are essential to counteract increasing antibiotic resistance world-wide. One such alternative strategy is to target and inhibit a pathogen's virulence machinery. Listeria monocytogenes is a food-borne Gram-positive bacterial pathogen involved in major outbreaks every year, causing listeriosis especially among pregnant women, the immunocompromised, and other at-risk individuals. The intracellular lifecycle of L. monocytogenes is well studied, making it an excellent model species for the targeting of specific virulence pathways. One of the major virulence regulators is the transcriptional regulator PrfA (Positive regulatory factor A), a member of the Crp/Fnr family of regulators that bind DNA through the helix-turn-helix motif. Published data suggest that PrfA requires the binding of a co-factor, glutathione GSH, for full activity, and from the crystal structures of PrfA in complex with GSH, and in complex with GSH and its cognate DNA, the hlv operator PrfA-box motif we revealed the structural basis for a GSH-mediated allosteric mode of activation of PrfA in the cytosol of the host cell (1). Furthermore we describe structure-guided design and synthesis of a set of PrfA inhibitors based on ring-fused 2-pyridone heterocycles (2,3). Our most effective compound decreased virulence factor expression, reduced bacterial uptake into eukarvotic cells, and improved survival of chicken embryos infected with L. monocytogenes compared to previously identified compounds. Crystal structures identified an intra-protein "tunnel" as the main inhibitor binding site (A₁), where the compounds participate in an extensive hydrophobic network that restricts the protein's ability to form functional DNA-binding HTH motifs. Our studies also revealed a hitherto unsuspected structural plasticity of the HTH motif. In conclusion, we have designed 2-pyridone analogues which function as site-A1 selective PrfA inhibitors with potent anti-virulence properties.

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Keywords: Antibiotic resistance, drug design, PrfA, structureactivity relationship

MS06 molecular machines and big complexes

Chairs: Prof. Guillermo Montoya, Prof. Kristina Djinovic Carugo

MS06-01

Unveiling (class III) transcription through integrative structural biology

Alessandro Vannini1

1. Division of Structural Biology, The Institute of Cancer Research, London, United Kingdom

email: alessandro.vannini@icr.ac.uk

RNA Polymerase (Pol) III is the eukaryotic nuclear enzyme devoted to the transcription of essential non-coding RNAs, including the entire pool of tRNAs, the 5S ribosomal RNA and the U6 spliceosomal RNA. Yeast Pol III comprises 17 subunit and accounts for approximately 750 kDa in mass.

Initiation of gene transcription by RNA Pol III requires the activity of TFIIIB, a complex formed by Brf1, TBP and Bdp1. TFIIIB is required for recruitment of Pol III and to promote the transition from a closed to an open Pol III pre-initiation complex (PIC), a process stimulated by the activity of the Bdp1 subunit. Here we present two cryo-EM reconstruction of an open RNA Pol III PIC at 3.8Å and 3.3 Å, and a reconstruction of RNA Pol III at 3.0 Å.

The structures presented unravel the molecular mechanisms underlying RNA Pol III transcription initiation, highlighting the specific features of this highly efficient essential machinery but also the general conserved mechanisms of gene transcription initiation.

We also present the crystal structures of a vertebrate specific TFIIIB complex, containing the Brf2 subunit, a protein overexpressed in lung and breast cancers. Brf2 encompasses a redox-sensing switch, capable of turning on and off transcription of target genes in a redox dependent manner. Integrating structural and biochemical and functional data in living cells we discovered Brf2 to act as a master switch of the oxidative stress response and establish a mechanistic link between Brf2-dependent Pol III transcription and cancer.



Keywords: RNA Polymerase III, x-ray crystallography, cryo-EM

MS06-O2

A hub for 3'-end processing: structural insights into mrna polyadenylation

Ana Casañal¹

1. MRC-Laboratory of Molecular Biology, Cambridge, United Kingdom

email: acasanal@mrc-lmb.cam.ac.uk

Almost all eukaryotic pre-mRNAs must undergo 5' capping, splicing and 3'-end processing before they can be transported to the cytoplasm for their translation into proteins. 3'-end processing involves over 20 different protein factors that also co-ordinate transcription termination. The cleavage and polyadenylation factor (CPF) is an essential component of the 3'-end machinery that cleaves pre-mRNA transcripts and adds the 3' polyA tails. Despite its fundamental importance, we are still far from understanding the molecular mechanisms of CPF. Here, we identify a sub-complex of the yeast CPF, the polyadenylation module (pAm), which acts as a hub for protein-protein interactions. Using cryo-EM we determine a 3.5 Å structure of the Cft1-Pfs2-Yth1 subunits of pAm. This consists of 4 beta propellers in Cft1 and Pfs2 that are strikingly similar to other interaction hubs involved in DNA and RNA processing. The zinc finger Yth1 protein extends from the side, providing an RNA binding surface. Biochemical studies confirm the structural observations and indicate the important role of pAm as the scaffold element of CPF to assemble other CPF subunits, including the poly(A) polymerase, and accessory factors of the 3'end processing machinery on RNA. We now aim to understand how the enzymatic activities are regulated. Our most recent results will be presented.

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Keywords: cryo-EM, RNA processing, polyadenylation

MS06-O3

Structural insights into the recognition between tri-ubiquitin and ubiquitin binding protein

Yu-Chih Lo1, Lin Shan-Meng1, Lin Su-Chang2

- Department of Biotechnology and Bioindustry Sciences, College of Bioscience and Biotechnology, National Cheng-Kung University, Tainan, Taiwan
- 2..Genomic Research Center, Academia Sinica, Taipei, Taiwan

email: grace.ncku@gmail.com

Poly-ubiquitin chains are important signaling molecules that were assembled by the ubiquitination process in order to trigger different linkage-specific signaling pathways through subsequent protein-protein interaction with downstream signaling molecules. The K63 and linear polyubiquitins are involved in non-degradative signaling pathways that mostly regulate the NF-kB activation and tumor necrosis factor receptor (TNFR)-mediated cell death, as well as necroptosis, in which deubiquitinases play a significant role in deciphering ubiquitin codes for regulating signaling. However, the molecular mechanism of how a polyubiquitin chain recognizing signaling molecules remains unclear. Emerging evidence in recent years shows that A20, a deubiquitinase, down-regulates the NF-kB activation signaling by interacting and degrading the polyubiquitin chains. The interaction is mediated by A20-binding inhibitors of NFkB, ABINs, which contain both A20 and linear polyubiguitin interacting domains. Here we report our recent works on the ABIN2:polyubiquitin complex. Structural analyses together with the mutagenesis, pull-down, and isothermal titration calorimetry assays show that ABIN2 has a primary and a secondary linear ubiquitin-binding site. Surprisingly, a tri-ubiquitin molecule could simultaneously interact with two ABIN2 dimers, in which the ubiquitins form a helical trimer when bridging two hABIN2 dimers. Our studies suggest the formation of a higher-order complex between a linear polyubiquitin chain, ABIN2, and A20.

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Keywords: Ubiquitin, Ubiquitin Binding Proteins, Protein Complex, Crystal Structure

MS06-O4

The structural biology of mitochondrial respiratory complex assembly

Megan Maher¹, Shadi Maghool¹, Anuradha Herath¹, Saumya Udagedara¹, David Dougan¹, David Stroud², Michael Ryan³, Kaye Truscott¹

- 1. La Trobe Institute for Molecular Science, La Trobe University, Melbourne, Australia
- The Bio21 Molecular Science and Biotechnology Institute, University of Melbourne, Melbourne, Australia
- Department of Biochemistry and Molecular Biology, Monash Biomedicine Discovery Institute, Monash University, Melbourne, Australia

email: m.maher@latrobe.edu.au

The mitochondrial oxidative phosphorylation system generates the bulk of cellular ATP, fuelling the energy demands of most eukaryotes. Five multi-subunit protein complexes in the mitochondrial inner membrane, termed complexes I to V, comprise the oxidative phosphorylation system. Many of these complexes require redox active cofactors, such as metal atoms and flavin for activity. The enzyme cytochrome c oxidase (CcO; Complex IV), which is the terminal oxidase of the mitochondrial respiratory chain requires three copper ions for assembly and activity of the complex. Succinate: quinone oxidoreductase (SOR; Complex II) functions in energy metabolism, coupling the tricarboxylic acid cycle and electron transport chain in bacteria and mitochondria and requires covalent incorporation of the cofact FAD for activity. The biogenesis of flavinylated SdhA, the catalytic subunit of SOR, is assisted by a highly conserved assembly factor termed SdhE in bacteria.

The protein Coa6 is located in the intermembrane space of mitochondria and is required for CcO assembly, with a suggested a role in the Cu-delivery pathway to CcO [1]. Our recent work has shown that Coa6 binds Cu(I), however the mechanism of how Coa6 mediates Cu-delivery is unknown. Studies on a clinically-relevant mutation of the Coa6 protein, C59W, have proposed that the mutation acts to disrupt protein-protein interactions between Coa6 and its proposed protein partners with identified roles in CcO assembly, leading to dysfunctions in Cu incorporation into CcO [3].

This presentation will describe the crystal structure of the native Coa6 and W59C mutant proteins and implications for the role of this protein in CcO assembly. The structure of *Escherichia coli* SdhE in complex with SdhA will also be described, which provides a structural explanation for the loss-of-function mutation, Gly78Arg, in SDHAF2, which causes hereditary paraganglioma 2 [4].

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Keywords: mitochondria, assembly, respiratory complex

MS06-O5

The Structural Organization of Substrate Loading in Iterative Polyketide Synthases

Roman Jakob¹, Dominik A. Herbst¹, Callie R. Huitt-Roehl², Jacob M. Kravetz², Philip A. Storm², Jamie R. Alley², Craig A. Townsend², Timm Maier¹

- 1. Department of Biozentrum, University of Basel, Basel, Switzerland
- 2. Department of Chemistry, Johns Hopkins University, Baltimore, United States of America

email: roman.jakob@unibas.ch

Polyketide synthases (PKSs) are microbial multienzymes for the biosynthesis of biologically potent secondary metabolites. Polyketide production is initiated by the loading of a starter unit onto an integral acyl carrier protein (ACP) and its subsequent transfer to the ketosynthase (KS). Initial substrate loading is achieved either by multidomain loading modules or by the integration of designated loading domains, such as starter unit acyltransferases (SAT), whose structural integration into PKS remains unresolved. A crystal structure of the loading/condensing region of the nonreducing PKS CTB1 demonstrates the ordered insertion of a pseudodimeric SAT into the condensing region, which is aided by the SAT-KS linker. Cryo-electron microscopy of the post-loading state trapped by mechanism-based crosslinking of ACP to KS reveals asymmetry across the CTB1 loading/-condensing region, in accord with preferential 1:2 binding stoichiometry. These results are critical for re-engineering the loading step in polyketide biosynthesis and support functional relevance of asymmetric conformations of PKSs

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Keywords: mechanism-based crosslinking, multidomain loading modules, natural products

MS07 Nucleic acids and interactions with proteins

Chairs: Prof. Ralf Ficner, Prof. Markus Wahl

MS07-01

Structure and function of the spliceosome

Rui Zhao¹, Xueni Li¹, Shiheng Liu², Lingdi Zhang¹, Jiansen Jiang², Sara Espinosa¹, Ryan Hill¹, Kirk Hansen¹, Hong Zhou²

- 1. Biochemistry and Molecular Genetics, Aurora, United States of America
- 2. Electron Imaging Center for Nanomachines, Los Angeles, United States of America

email: rui.zhao@ucdenver.edu

Pre-mRNA splicing is catalyzed by the spliceosome, a huge protein-RNA complex composed of the U1, U2, U4, U5, U6 snRNPs and many non-snRNP related proteins. U1 sn-RNP plays a critical role in 5' splice site recognition and is a frequent target of alternative splicing factors. These factors transiently associate with human U1 snRNP and are not amenable for structural studies, while their Saccharomyces cerevisiae (yeast) homologs are stable components of U1 snRNP. We have recently determined the structure of yeast U1 snRNP at 3.6Å resolution using cryoEM. The structure reveals common features as well as important differences from the human U1 snRNP. It provides atomic models of nearly all essential domains of U1 snRNA, all core proteins, and five auxiliary proteins. The structure offers a framework to integrate a wealth of existing genetic and biochemical data regarding the structure and function of yeast U1 sn-RNP and the mechanism of 5' ss recognition. In addition, the yeast U1 snRNP structure and biochemical analyses based on the structure provided intriguing insight into the structure and function of these auxiliary human U1 snRNP proteins in alternative splicing in higher eukaryotes.

The spliceosome undergoes dramatic changes signified by the E, A, Pre-B, B, Bact, B*, C, C*, P, and ILS complexes in a splicing cycle. CryoEM structures of B, Bact, C, C*, and ILS revealed mechanisms of 5' ss recognition, branching, and intron release, but lacked information on 3' ss recognition. exon ligation and release, all related to the post-catalytic P complex. We have recently determined the cryoEM structure of the yeast P complex at 3.3Å resolution, revealing that the 3' ss recognition is driven by the interaction between 3' and 5' ss, likely facilitated by a stem-like structure formed in the intronic regions between the branch site and 3' ss. The structure shows that a new protein(s) becomes stably associated with the core components of the P complex around Prp8 and Prp22, securing the 3' exon and potentially regulating the activity of Prp22. The structure demonstrates that Prp22 binds 15-21 nucleotides downstream of the exon-exon junction, enabling it to pull the 3' intron-exon and ligated exon in a 3' to 5' direction to achieve 3' ss proofreading and exon release, respectively. By providing insights into the 3' ss recognition, exon ligation, and the action of RNA helicase Prp22, the P complex structure fills a major gap in our understanding of the splicing cycle.

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Keywords: spliceosome, cryo EM, alternative splicing

MS07-O2

Post-translational regulation of gene expression in the immune system by Roquin/RC3H1 and ribonucleases of the Regnase/ZC3H12/MCPIP family

Udo Heinemann¹, Ankur Garg¹, Yvette Roske¹, Anja Schütz²

- 1. Crystallography, Max Delbrück Center for Molecular Medicine, Berlin, Germany
- Protein Sample Production Facility, Max Delbrück Center for Molecular Medicine, Berlin, Germany

email: heinemann@mdc-berlin.de

Roquin/RC3H1 and Regnase/ZC3H12/MCPIP family members control the lifetime and degradation of their target mRNAs by binding to characteristic stem-loop structures in their 3'-untranslated regions (3'UTRs). In earlier work [1] we have determined the crystal structure of the ROQ domain of human Roquin-1 and characterized its binding to constitutive decay elements (CDEs) present in the 3'UTRs of tumor necrosis factor-α (TNF-α) and the inducible T-cell co-stimulator (ICOS) mRNA. Roquin-1 was shown to post-transcriptionally regulate the A20 mRNA, thereby modulating the activity of the IKK/NF-kB pathway [2]. Roquin-1 mediates mRNA degradation by recruiting the CCR4-CAF1-NOT deadenylase complex to mRNAs after CDE binding. Closely similar stem-loop structures are recognized by the Regnase enzymes that mediate mRNA breakdown through their intrinsic ribonuclease activity. These enzymes share a PIN-type ribonuclease domain followed by a unique CCCH zinc-finger (ZnF) domain. In recent work, we have determined crystal structures of the Regnase-3 PIN domain and of a heptaribonucleotide bound to a Regnase-3 fragment containing both the PIN and the ZnF domain. These structures reveal binding modes of the RNA to both the PIN domain and the zinc finger of Regnase-3 and suggest a basis for RNA loop recognition by the unique zinc finger. In addition, we discovered - by serendipity - a novel form of double-stranded RNA incorporating a half-turn of A-like RNA based entirely on wobble-base pairing, which we termed W-RNA [3]. The W-RNA formed under acidic crystallization conditions from oligonucleotides expected to form CDE-like RNA stem-loops and is stabilized by C-A+ wobble-base pairing. We propose that RNA duplexes based on pH-switchable wobble-base pairing may find biotechnological applications in the future.

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Keywords: post-translational regulation, RNA-binding protein, protein and RNA structure

MS07-O3

Molecular mechanism of the TP901-1 lysogeny switch

Leila Lo Leggio¹, Kim K. Rasmussen¹, Anders K. Varming¹, Kristian E.H. Frandsen¹, Peter W. Thusltrup¹, Mogens Kilstrup², Karin Hammer², Malene R. Jensen³

- 1. Department of Chemistry, University of Copenhagen, Copenhagen, Denmark
- 2. DTU Bioengineering, Technical University of Denmark, Kgs. Lyngby, Denmark
- 3. Univ. Grenoble Alpes, CNRS, CEA, IBS, Grenoble, France

email: leila@chem.ku.dk

Bacteriophages are bacterial viruses which can be classified as lytic (virulent) or lysogenic (temperate). Lytic bacteriophages synthesize new progeny directly after infection, whereas lysogenic phages can enter the alternative lysogenic life cycle, where the phage DNA integrates in the bacterium's genome until prompted to switch to the lytic cycle by an external signal. The potential of phages in the fight against antibiotic resistance and increasing understanding of their roles in bacterial pathogenicity have recently rekindled research interest in these diverse and extremely widespread entities.Lysogeny switches have been some of the first models of genetic regulation, but despite superficial similarities, the molecular basis of different switches are rather different.

In the dairy industry, phages of lactic acid bacteria are extremely detrimental. Within the last ten years, we have studied the structural biology of the Lactococcus lactis TP901-1 lysogeny switch through an integrative structural biology approach combining biochemistry, crystallography, NMR and CD spectroscopy and small angle scattering. At the DNA level the lysogeny switch of TP901-1 consists of some operator sites and the two genes cI and mor; under the control of two divergent promoters, and coding for the two main regulatory proteins. The repressor CI, alone sufficient to establish lysogeny, consists of an N-terminal DNA binding domain (NTD) of the HTH type (1) connected by a flexible linker (2) to a helical hooks dimerization region (CTD₁) (3) and an additional helical region which mediates hexamerization (CTD₂). A dimeric truncated form binds to each of three palindromic operator sites (O_R , O_L and O_D), by binding to adjacent half-sites (3), while the hexamer is thought to bind simultaneously to all three operators, repressing the lytic life cycle promoter (P_1) . We are pursuing the structure of full-length CI/DNA complex by small angle neutron scattering (SANS). The anti-repressor MOR has previously been suggested to bind to CI, forming a complex, which binds to a still unknown DNA sequence in order to repress the lysogenic life cycle promoter (P_R) . We recently determined the structure of MOR and its complex with the NTD region of CI, and are further investigating is binding to a composite DNA binding site by biochemical methods and SANS, to give us a full understanding of the function of this simple but efficient switch. As an additional perspective, the interaction of MOR with CI-NTD in TP901-1 is expected to be conserved in putative switches of S. aureus phages, which are also under investigation.

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Keywords: Bacteriophage, genetic switch, repressor/ antirepressor

MS07-O4

Crystal structure of TraN, a regulator of conjugative DNA-transfer, in complex with its cognate DNA binding site

Walter Keller¹, Verena Kohler¹, Nikolaus Goessweiner-Mohr¹, Andreas Aufschnaiter¹, Christian Fercher², Ines Probst³, Tea Pavkov-Keller¹, Kristin Hunger¹, Heimo Wolinskiv¹

- 1. Institute of Molecular Biosciences, University of Graz, Graz, Austria
- Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane, Australia
- Division of Infectious Diseases, University Medical Center Freiburg, Freiburg, Germany

email: walter.keller@uni-graz.at

Bacterial conjugation is the most prevalent route of DNA transfer between bacteria and mediates the rapid spread of bacterial resistances within bacterial communities. Type IV secretion system (T4SS), elaborate molecular machines, are responsible for the efficient transport of nicked, single-stranded plasmid DNA across the cell walls of the donor as well as the recipient cell [1]. We investigate the T4SS from the antibiotic resistance plasmid pIP501, which is encoded within a single operon comprised of 15 putative transfer factors. The 14th open reading frame encodes TraN, a specific double-strand DNA binding protein, which recognizes a 34 bp long stretch of DNA positioned 72 bp upstream of the oriT nick site [2]. The structure of unbound TraN has been determined previously [2]. Here we present the TraN-DNA complex structure determined at 1.93 Å and show that TraN acts as a repressor of the pIP501 encoded T4SS. The repressor function of TraN has been shown in in vivo experiments: an E. faecalis traN deletion strain exhibits highly increased transfer rates, as well as elevated mRNA and protein levels of the all tested tra-operon components, including the putative T4SS complex member TraM. Based on the detailed analyses of the TraN-DNA interaction we identified a further high-affinity binding site within the tra-operon (upstream of the traN gene). Furthermore, we show that related plasmids of the Inc18 family that encode a TraN homolog also harbor at least one conserved TraN binding site. We therefore conclude that the proposed regulatory role of TraN is conserved in the related plasmids.

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Keywords: Type 4 Secretion Systems, Repressor, antibiotic resistance

MS07-O5

RNA specificity of NHL domains revisited: LIN-41/TRIM71 binds a defined RNA stem-loop element via shape and electrostatic complementarity

Heinz Gut¹, Pooja Kumari¹, Florian Aeschimann¹, Dimos Gaidatzis¹, Jeremy J. Keusch¹, Anca Neagu¹, Katarzyna Pachulska-Wieczorek², Helge Grosshans¹, Rafal Ciosk¹

- 1. Friedrich Miescher Institute for Biomedical Research, Basel, Switzerland
- 2. Institute of Bioorganic Chemistry, Polish Academy of Sciences, Poznan, Poland

email: heinz.gut@fmi.ch

RNA-binding proteins regulate a myriad of biological pathways by tightly controlling the fate of ribonucleic acids. For this purpose, nature has evolved an arsenal of different RNA binding domains specialized to specifically associate with a variety of target RNAs. While some of these protein domains show preference for a defined RNA sequence motif, others interact primarily with structured RNA elements. For both cases, examples for recognition of single-stranded or double-stranded RNA stretches have been identified. Only very recently, the NHL domain of TRIM-NHL protein family members, which include some of the key regulators of cell proliferation and differentiation, has been added to the repertoire of RNA-binding folds. The TRIM-NHL family member Brat from Drosophila melanogaster has been shown to specifically bind, via its NHL domain, a short single-stranded RNA stretch containing a defined sequence motif [1]. However, it remains largely unexplored how the many other family members featuring the WD40-like beta-propeller of the NHL domain interact with RNA. Here we present a completely different solution for recognition of an RNA element by the NHL domain of another TRIM-NHL family member. The Caenorhabditis elegans LIN-41 protein, a well-studied target of the let-7 miRNA, regulates developmental processes in the soma and has been shown to reprogram germ cells into pluripotency during the oocyte to embryo transition. Similarly, its human homolog TRIM71 plays a role in cellular plasticity by regulating the transition from differentiated to pluripotent cells. In both worms and mammalian cells, LIN-41/TRIM71 function has been linked to degradation or translational repression of specific mRNAs, but how these RNA molecules are recognized has remained a mystery [2]. By combining computational analysis, X-ray crystallography, and in vivo studies in worms and human cells, we find that the NHL domain of LIN-41/TRIM71 binds a short stem-loop RNA element, which is present in multiple copies in the 5'- or 3'-UTRs of well-established LIN-41/TRIM71 mRNA targets. Based on the computational and structural data, we suggest a LIN-41 RNA response element of varying sequences capable of folding into the correct 3D RNA-hairpin structure to achieve specificity by shape and electrostatic complementarity to a positively charged, shallow pocket in the NHL domain of LIN-41/TRIM71 [3].

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Keywords: RNA metabolism, NHL domain, X-ray crystallography

MS08 Membranes and membrane interacting proteins

Chairs: Prof. Susanna Törnroth-Horsefield, Prof. Adrian Goldman

MS08-O1

P-type ATPase inhibitors: something old, something new, leads to follow and some new clues

Maike Bublitz1

1, Department of Biochemistry, University of Oxford, Oxford, United Kingdom

email: maike.bublitz@bioch.ox.ac.uk

P-type ATPases are a widespread family of membrane pumps that mediate a plethora of essential cellular transport functions. Consequently, many P-type ATPases rank as prime drug targets, both in the context of human disorders and infectious diseases. The exploration of potent P-type ATPase inhibitors throughout the last decades has in turn strongly advanced our understanding of the molecular pumping mechanism that underlies substrate transport across lipid bilayers. One of the most widely used inhibitors in P-type ATPase research is vanadate, although structural details of its inhibitory mechanism have long remained unresolved. We have determined the crystal structure of the sarcoplasmic reticulum Ca2+-ATPase (SERCA) in complex with vanadate [1], allowing a description of its binding mode in the catalytic site, along with some novel insight into ion and nucleotide binding sites in SERCA. In addition to the phosphate-mimic vanadate, we have further identified a novel class of P-type ATPases inhibitors [2]. Using a set of rationally designed compounds, we have analyzed their structure-activity relationship by functional assays, crystallography and computational modeling. These new inhibitors are candidates for further development towards drugs against invasive fungal infections.

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 *contributed equally

Keywords: P-type ATPases, Membrane pumps, Inhibitory compounds

MS08-O2

Membrane transport by proteins of the 7+7 inverted repeat superfamily: variation on a theme

Alexander Cameron¹

1. University of Warwick, Coventry, United Kingdom

email: a.cameron@warwick.ac.uk

Secondary active membrane transport proteins specifically move molecules across membranes. As first posited by Jardesky in the 1960s, they work by the alternating access mechanism, in which the binding site of the protein is open alternately to one side of the membrane and then, through a conformational change, to the other. This enables the molecule to be carried across the membrane. Membrane transporters have been divided into families based on sequence and substrate specificity. Over the last decade many structures have been solved of proteins from different families. Through these studies it has been seen that, though the topology of the proteins varies, they often contain inverted repeats and these repeats have been implicated in the transport mechanism. Two of the more recent structures we solved, the human anion exchanger 1¹ and the uric acid/xanthine H(+) symporter, UapA from Aspergillus *nidulans*², both have a 7 + 7 inverted repeat. I will discuss the mechanisms of these two proteins and how they compare to other membrane transport proteins that we have solved previously.

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Keywords: Membrane transport proteins, mechanism
MS08-O3

What we have learned about membranebound pyrophosphatases (mPPases) from X-ray crystallography, MD simulations, FRET and PELDOR

Steven Harborne¹, Nita Shah¹, Craig Wilkinson¹, Christos Pliotas², Sarah Harris¹, Roman Tuma¹, Adrian Goldman¹

- 1. Astbury Centre for Structural Molecular Biology. University of Leeds, Leeds, United Kingdom
- 2. University of St Andrews, St Andrews, United Kingdom

email: mba07sh@gmail.com

Membrane-bound pyrophosphatases (mPPases) couple the hydrolysis of inorganic pyrophosphate to the pumping of ions (sodium or protons) across a membrane in order to generate an electrochemical gradient. This class of membrane protein is widely conserved across plants, fungi, archaea and bacteria, but absent in multicellular animals. The absence of mPPases from higher eukaryotes makes them an attractive drug target against protozoan parasites such as Plasmodium falciparum and pathogens such as Bactoroides vulgatus [1]. During one catalytic turnover, an mPPase must bind its substrate (PP_i), pump an ion(s) across the membrane, hydrolyze PP; and release 2P; as product. The mPPases of different species differ in respect to the ion they pump, either sodium, protons or both; and they display varying dependence on potassium ions. We have used X-ray crystallography to solve numerous structures of the Thermotoga maritima mPPase, providing us with snapshots of the protein throughout the catalytic cycle and an excellent understanding between three-dimensional structure and enzyme function [2]. Some questions still remain, including the molecular details of potassium dependence for catalysis, and residues involved in defining single-pumping versus dual-pumping of sodium ions and protons. We also wanted to explore the dynamics and kinetics of the catalytic cycle between the static snapshots afforded to us by crystallography. We employed molecular dynamics (MD) simulation [3], pulsed electron-electron double resonance (PELDOR/DEER) and single-molecule Förster resonance energy transfer (FRET) measurements to determine the dynamic range and frequency of conformations available to the enzyme in a lipid bilayer during the catalytic cycle, leading to further insights into the mechanism of this enzyme.



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Keywords: membrane protein, MD simulation, FRET

MS08-O4

Structural and functional studies on a prokaryotic homologue of the mammalian SLC7 cationic amino acid transporters

Katharina Jungnickel¹, Joanne Parker², Simon Newstead²

- The Hamburg Centre for Ultrafast Imaging (CUI) & Department of Chemistry, Institute of Biochemistry and Molecular Biology, Hamburg, Germany
- 2. Department of Biochemistry, University of Oxford, Oxford, United Kingdom

email: Katharina.Jungnickel@chemie.uni-hamburg.de

The Amino acid/Polyamine/Cationic (APC) superfamily is among the largest of the secondary active transporters. Members of the APC superfamily are responsible for the uptake of amino acids and other substrates using either a proton or sodium gradient to drive substrate translocation across the membrane. Since Amino acids, and their derivatives, are crucial for both prokaryotic and eukaryotic cell biology, the systems responsible for their transport are important targets.

In particular, cationic amino acid transporters (CATs), members of the solute carrier (SLC) family 7, determine the availability of arginine in the cell. Arginine is the precursor for L-ornithine and nitric oxide (NO) synthesis and thus an important cellular signalling molecule as well as a proposed major regulator of the mTORC1 pathway.

Here, the crystal structure of a proton-coupled amino acid transporter closely related to the SLC7 family, from *Geobacillus kaustophilus, Gk*ApcT, is presented. To study the transport mechanism of *Gk*ApcT, liposome-based functional assays were performed to characterise the substrate specificity and kinetics. Additionally, the crystal structure guided a detailed site-directed mutagenesis study, which identified several conserved residues involved in substrate binding and proton-coupling. The current structure served as a template understand proton-coupled amino acid transport in bacteria, and to understand mammalian amino acid transport by the SLC7 family.

Keywords: SLC7, amino acid transporters, membrane protein

MS08-O5

The structure of RVFV fusion protein reveals a lipid binding pocket conserved in class-II fusion proteins

Pablo Guardado Calvo¹, Kalina Atkovska², Jochen Hub², Felix Rey¹

- 1. Department of Virology, Institut Pasteur, Paris, France
- 2. Institute for Microbiology and Genetics, University of Goettingen, Goettingen, Germany

email: guardado@pasteur.fr

The Rift Valley fever virus (RVFV), a member of the genus Phlebovirus within the order Bunyavirales, is an arthropod-borne virus (arbovirus) responsible for epizoonoses throughout Africa with devasting economic consequences and causing serious disease in humans. The fact that RVFV can be transmitted to humans by multiple mosquito species, a number of which are spread across the planet, is a source of considerable concern. RVFV virions display two envelope proteins at their surface, Gn and Gc, associated as heterodimers arranged with icosahedral symmetry. The virus enters cells via receptor-mediated endocytosis, with glycoprotein Gc catalyzing the acid-induced membrane fusion reaction with the endosome for entry. The structure of Gc in prefusion conformation showed the characteristic fold of class II membrane fusion proteins, initially identified in other arboviruses, such as those in the genus Flavivirus (zika, dengue and yellow fever viruses) and in the genus Alphavirus (which includes among others the pathogenic chikungunya virus).

We have solved the structure of RVFV fusion protein (Gc) in its post-fusion conformation in complex with a lipid (phosphatidylcholine) bound in a pocket near the fusion loop, which is the region responsible to interact with cellular membranes. Membrane binding experiments showed that Gc requires specific glycerophospholipids (GPL) and cholesterol for binding to target membranes and the X-ray structure, together with site directed mutagenesis and molecular dynamics simulations, reveals the molecular determinants of this specificity [1]. Strikingly, the GPL head group recognition pocket is conserved in the fusion proteins of other arthropod-borne viruses, such as zika, dengue or chikungunya viruses, which have recently caused major epidemics worldwide. Indeed, the membrane-insertion mechanism identified in this work helps us to understand the changes in cholesterol dependence linked to a serious outbreak of Chikungunya virus in 2005-2006 and the phosphatidylserine dependence of Dengue virus for entry. Moreover, the identified pocket will represent a new target for the development of antivirals against a broad range of pathogenic arbovirus (flavivirus, alphavirus and bunyavirus).

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 Guardado-Calvo, P., et al., A glycerophospholipid-specific pocket in the RVFV class II fusion protein drives target membrane insertion. Science, 2017. 358(6363): p. 663-667.Keywords: membrane fusion, class-II fusion proteins, bunyavirus

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MS09 Enzymology

Chairs: Prof. Leila Lo Leggio, Dr. Dusan Turk

MS09-01

Kinetic X-ray crystallography to watch proteins in action

Martin Weik1

1. Institut de Biologie Structurale, Grenoble, France

email: weik@ibs.fr

Kinetic X-ray crystallography permits the structural characterization of macromolecular conformational changes along a reaction pathway at the atomic level of spatial resolution. After triggering the biological reaction within a macromolecular crystal, functionally relevant conformational changes are either arrested by flash-cooling the crystal, allowing characterization of the structure by conventional cryo-crystallography (intermediate trapping), or followed in real time by time-resolved crystallography at room temperature. The temporal resolution of the latter is limited to 100 ps if carried out in the form of Laue crystallography at synchrotrons. The advent of X-ray free electron lasers (XFELs) has pushed the resolution to the sub-ps regime, allowing ultrafast changes to be studied by time-resolved serial femtosecond crystallography. We will illustrate the cryo-trapping approach by following product release in an insect carboxylesterase that hydrolyses organophosphates [1]. Radiolytic cleavage of the bond between the active-site serine and the organophosphate is observed at 150 K but not at 100 K. The increased solvent and protein mobility at 150 K is thus required to allow for product release and accompanying protein conformational changes to occur. Time-resolved crystallography will be exemplified with the study of ultra-fast photoswitching in a fluorescent protein from a non-fluorescent (off) to a fluorescent (on) state further to excitation by a light flash [2]. Our consortium (see author list of [2]) has employed time-resolved serial femtosecond crystallography at an XFEL to identify the transient structure of the photoswitchable fluorescent protein rsEGFP2 in its excited state, and to observe its chromophore in a twisted conformation, midway between the stable configurations of the on and off states. This observation has been confirmed by simulations and has allowed to rationally design a mutant with a two-fold increased photoswitching quantum yield.

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Keywords: kinetc crystallography, XFEL, serial crystallography

MS09-O2

Structure, function, and inhibitors of the Helicobacter pylori acid acclimation system, an essential component for chronic infection

Hartmut Luecke1

1. Center for Molecular Medicine, University of Oslo, Oslo, Norway

email: hudel@ncmm.uio.no

Half the world's population is chronically infected with Helicobacter pylori, causing gastritis, gastric ulcers and an increased incidence of gastric adenocarcinoma. Its proton-gated inner-membrane urea channel, HpUreI, is essential for survival in the acidic environment of the stomach. The channel is closed at neutral pH and opens at acidic pH to allow the rapid access of urea to cytoplasmic urease. Urease produces NH₃and CO₂, neutralizing entering protons and thus buffering the periplasm to a pH of roughly 6.1 even in gastric juice at a pH below 2.0. Here we report the structure of HpUreI, revealing six protomers assembled in a hexameric ring surrounding a central bilayer plug of ordered lipids. Each protomer encloses a channel formed by a twisted bundle of six transmembrane helices. The bundle defines a previously unobserved fold comprising a two-helix hairpin motif repeated three times around the central axis of the channel, without the inverted repeat of mammalian-type urea transporters. Both the channel and the protomer interface contain residues conserved in the AmiS/ UreI superfamily, suggesting the preservation of channel architecture and oligomeric state in this superfamily. Predominantly aromatic or aliphatic side chains line the entire channel and define two consecutive constriction sites in the middle of the channel. The novel hexameric channel structure provides a new paradigm for the permeation of urea and other small amide solutes in prokaryotes and archaea. Our high-throughput screens have identified sub-micromolar inhibitors of H. pylori's acid acclimation system. Follow-up microsecond-scale unrestrained molecular dynamics studies provide a detailed mechanism of urea and water transport by HpUreI. In parallel we have determined the structure of the 1.1 MDa cytoplasmic urease complex by cryo EM to 3.1 Å resolution.



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MS09-O3

Structure determination of lytic polysaccharide monooxygenases interactions with substrate

Tobias Tandrup¹, Kristian E. H. Frandsen¹, Thomas J. Simmons², Jens-Christian N. Poulsen¹, Louis F.L. Wilson², Jens-Christian N. Poulsen¹, Katja S. Johansen³, Paul Dupree², Leila Lo Leggio¹

- 1. Department of Chemistry, University of Copenhagen, Copenhagen, Denmark
- 2. Department of Biochemistry, University of Cambridge, Cambridge, United Kingdom
- 3. Department of Geoscience and Natural Resources Management, University of Copenhagen, Copenhagen, Denmark

email: tobias.tandrup@live.dk

Lytic Polysaccharide Monooxygenases (LPMOs) are copper-dependent enzymes discovered within the last ten years, which oxidatively degrade recalcitrant polysaccharides of the plant cell wall, making chains available for further degradation by hydrolytic enzymes. LPMOs show great potential as a key component in formulation of efficient enzyme cocktails for biomass conversion, and as such, for the production of bioethanol [1]. Very little experimental information on the interactions of LPMOs with their substrates was available until recently. A combined biochemical, crystallographic and spectroscopic study elucidated the interactions between a family AA9 LPMO of the filamentous fungus *Lentinus similis* (LSAA9A) and cellooligosaccharides [2].

More recently we have focused on a detailed comparative study of the substrate interactions and activity of *Ls*AA9A and *Collariella virescens* (*Cv*AA9A)[3]. In this presentation we will focus on the interactions of the LPMOs with cellooligosaccharides and hemicelluloses studied by X-ray crystallography. We thank the CESBIC consortium for initiating this project, and the Novo Nordisk foundation HOPE project (grant number: NNF17SA0027704).



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Keywords: Lytic Polysaccharide Monooxygenase, Complex structures, Cellooligosaccharides.

Keywords: Helicobacter pylori, HpUreI, Structure

MS09-O4

Structure and mechanism of C-acyltransferase from pseudomonas protegens

Tea Pavkov-Keller¹, Nina G. Schmidt², Anna Żądło-Dobrowolska³, Wolfgang Kroutil⁴, Karl Gruber⁵

- 1. University of Graz, Institute of Molecular Biosciences and ACIB, Graz, Austria
- University of Graz, Institute of Chemistry and ACIB, Graz, Austria
- 3. University of Graz, Institute of Chemistry, Graz, Austria
- University of Graz, Institute of Chemistry and BioTechMed, Graz, Austria
- University of Graz, Institute of Molecular Biosciences and BioTechMed, Graz, Austria

email: tea.pavkov@uni-graz.at

C-C bond forming reactions are the key transformations to set up the carbon framework of organic molecules. In this sense, the Friedel-Crafts acylation is commonly used for the synthesis of aryl ketones, that are motifs in many fine chemicals and natural products. Although various types of catalysts have been described for this reaction, a biocatalytic version, which may benefit from the chemo- and regioselectivity of enzymes, has not yet been introduced. Here, we describe a bacterial multi-component C-acyltransferase from Pseudomonas protegens that can catalyze Friedel-Crafts C-acylation of phenolic substrates in buffer without the need of CoA-activated reagents reaching up to >99% conversion [1,2]. We determined x-ray crystal structures of the complex using diffraction data from two different crystal forms at 2.8 and 3.4 Å resolution, respectively. This multimeric enzyme consists of three subunits - PhIA, PhIB and PhIC. They are arranged in a PhI(A2C2)2B4 composition, in which the four copies of PhIB mediate the binding of two PhIA and two PhIC dimers to form the complete oligomer. Soaking the native donor/acceptor monoacetylphloroglucinol into crystals of ATase and solving the complex structure revealed together with mutations that only residues from PhIC interact with the substrate, which indicates that this is the subunit responsible for the transferase activity we observed.

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Keywords: acyltransferase, multi-enzyme complex, Friedel-Crafts acylation

MS09-O5

Structural snapshots of multiple enzymeligand complexes pave the road for semi rational enzyme engineering

Zsofia Bata¹, Bence Molnár², Ibolya Leveles², Andrea Varga³, Csaba Paizs³, László Poppe¹, Beáta G. Vértessy²

- Budapest University of Technology and Economics, Department of Organic Chemistry and Technology, Budapest, Hungary
- Budapest University of Technology and Economics, Biostruct laboratory, Department of Applied Biotechnology and Food Science, Budapest, Hungary
- 3. Babeş-Bolyai University Faculty of Chemistry and Chemical Engineering, Cluj-Napoca, Romania

email: bata.zsofia@mail.bme.hu

Aromatic amino acid ammonia-lyases and 2,3-aminomutases contain the post-translationally formed prosthetic 3,5-dihydro-4-methylidene-5H-imidazol-5-one (MIO) group [1]. The so-called MIO-enzymes may be used for the sterooselective synthesis of enantiopure α - or β -amino acids, making these chemical processes more environmentally friendly and more affordable. Although, a number of structures are available in the PDB for MIO enzymes, the catalytically inportant Tyrloop [1] is either missing or is in a catalytically inactive conformation, due to the "loop-out" conformation in eukaryotic phenylalanine ammonia-lyase (PAL) structures (eg.: PDB:1W27 [2]). Lack of protein structure in a catalytically competent conformation impeded understanding the PAL mechanism and the key reasons for the enantioselectivity of the enzyme.

Our recent study characterized novel amino phosphonic acid inhibitors of MIO enzymes. [3] Enzyme kinetic measurements and isothermal titration calorimetry demonstrated that addition of a methylidene substituent to the β-carbon atom of the phosphonic acid analogue of the natural substrate, 1-Phe, enhanced binding (K_d = 40 nM) and reversed the enantiopreference of the enzyme. [3] Importantly, inhibitors characterized in this study, also facilitated the crystallization of PcPAL. The resulting refined structure is shown on Figure 1. It confirms the N-MIO catalytic mechanism and demonstrates that the strong binding of (S)-APPA is due to a covalent-like hydrogen bond between its phosphonic acids group and the catalytic Tyr110.

Further key insights were gained, as the protein also crystallized in complex with cinnamic acid, the product of the natural reaction, and d-phenylalanine, the non-reactive enantiomer. In addition we could also employ sodiumborohydride to reduce the MIO group, thus render the enzyme catalytically inactive without significantly distorting the active site geometry. Such reduced enzyme crystallized from the same conditions as the native enzyme in the presence of the natural substrate l-phenylalanine. Taken together these three new structures refine our understanding of the ligand binding modes and the catalytic mechanism of PcPAL. Moreover, analysis of the structures identified three key residue positions in the carboxyl-binding region that can be targeted for altering the enantioselectivity of the enzyme.

 Figure: Electron densities and modeled structure of the active site of PcPAL in complex with covalently bound but still reversible inhibitor (S)-APPA[3]. Unequivocally identifying the geometry of the bound ligand and the covalent bond formed (1.4 Å) with the MIO group. Resolution 1.9 Å.



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Keywords: catalytic mechanism, ligand binding, enzyme engineering

MS10 Hydrogen-bonding & weak interactions studied by neutrons and X-rays

Chairs: Prof. Marta E. G. Mosquera, Dr. Matthew Blakeley

MS10-O1

An aminophenothiazine inhibitor of the NCS-1/Ric8a complex regulates synaptic function in fragile X Syndrome

Maria Jose Sanchez-Barrena¹, Alicia Mansilla², Antonio Chaves-Sanjuán¹, Nuria Campillo³, Ourania Semelidou⁴, Loreto Martínez-González³, Efthimios Skoulakis⁴, Alberto Ferrús², Ana Martínez³

- Departamento de Cristalografía y Biología Estructural. Instituto de Química Física Rocasolano. CSIC, Madrid, Spain
- Dpto. de Neurobiología del Desarrollo. Instituto Cajal. CSIC, Madrid, Spain
- Dpto. de Biología Química y Física. Centro de Investigaciones Biológicas. CSIC, Madrid, Spain
- 4. Division of Neuroscience, Biomedical Sciences Research Centre Alexander Fleming, Vari, Greece

email: xmjose@iqfr.csic.es

The protein complex formed by the Ca2+ sensor neuronal calcium sensor 1 (NCS-1) and the guanine exchange factor protein Ric8a co-regulates synapse number and probability of neurotransmitter release, emerging as a potential therapeutic target for diseases affecting synapses such as Fragile X syndrome (FXS), the most common heritable autism disorder [1]. Using crystallographic data and the virtual screening of a chemical library [1,2], we identified a set of heterocyclic small molecules as potential inhibitors of the NCS-1/Ric8a interaction. The aminophenothiazine FD44 interferes with NCS-1/Ric8a binding and it restores normal synapse number and associative learning in a Drosophila FXS model [3]. The crystal structure of NCS-1 bound to FD44 and the structure-function studies performed with structurally close but inactive analogues explain the FD44 specificity and how this small compound can inhibit such big protein-protein interface: FD44 stabilizes NCS-1 in a conformation that impedes Ric8a recognition [3]. Our study demonstrates the druggability of the NCS-1/Ric8a interface and uncovers a suitable region in NCS-1 for development of additional drugs of potential use on FXS. In fact, we have combined the structural information obtained by X-ray crystallography, together with advanced computational methodologies to understand the basis of FD44 affinity and selectivity and find drug-like molecules with improved activity. Since other neuronal disorders share with FXS the synaptic density and morphology abnormalities, we believe that our compounds would be also useful for a whole range of synaptopathies, such as Rett Syndrome, autism, schizophrenia or bipolar disorder.

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Keywords: calcium sensor, molecular recognition, proteinprotein interaction

MS10-O2

Selective protonation and stereoelectronic effects govern catalysis in a pyridoxal-5'-phosphate-dependent enzyme

Andrey Kovalevsky1

email: kovalevskyay@ornl.gov

Pyridoxal-5'-phosphate (PLP, vitamin B₆ derivative) is one of the most ubiquitous co-factors in biological systems. At least 140 different types of biochemical transformations are catalyzed by PLP-dependent enzymes, comprising ~4% of all classified enzymatic activity. PLP-dependent enzymes perform some of the most difficult chemical reactions involving amines and amino acids, including transamination, racemization, phosphorylation, decarboxylation, aldol cleavage, elimination, and replacement reactions. PLP-dependent enzymes are categorized into five recognized fold-types (I-V), each performing characteristic chemistry. Despite decades of research, the physical determinants that govern specificity of and catalytic enhancement by PLP-dependent enzymes remain largely unresolved. Fold-type I is the most prevalent, mainly promoting transamination and decarboxylation reactions. Two major hypotheses have been developed to understand the different types of chemistry in PLP-dependent enzymes, namely 1) stereoelectronic control and 2) electronic modulation through selective protonation. An enzyme active site local environment can promote different protonation profiles of PLP during the catalytic cvcle. We report the first neutron crystal structure of a Fold I PLP-dependent enzyme, aspartate aminotransferase (AAT). In crystal, AAT was captured in both the internal and external aldimine states after soaking with substrate analog a-methyl-D-aspartic acid. The neutron structure illustrates the protonation state differences between the reactant (internal aldimine) and intermediate (external aldimine) states, and sheds new light on the catalytic mechanism of transamination. We are using QM/MM calculations and MD simulations based on the correct models derived from the neutron structure, and neutron vibrational spectroscopy for deeper understanding of the enzyme mechanism and to uncover the contribution of low-energy protein vibrations to catalysis.

Keywords: protonation, catalysis, dynamics

^{1.} Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, United States of America

MS10-O3

Structural, spectroscopic and physicochemical investigations of new cocrystals of diamines and alcohols

Grzegorz Cichowicz¹, Łukasz Dobrzycki¹, Roland Boese², Michal Cyrański¹

- 1. Faculty of Chemistry, University of Wasaw, Warsaw, Poland
- 2. Institute of Inorganic Chemistry, University of Duisburg-Essen, Duisburg, Germany

email: grzegorz.cichowicz@gmail.com

The aim of my study was to cocrystallize diamines, such as ethylenediamine and 2,2-dimethyl-1,3-propandiamine with various alcohols and determine structure of obtained systems. Both of the compound groups have enormous capabilities to form interesting structural motifs with many different substances. However in crystal structures of pure amines and alcohols there are often present chain motifs build by hydrogen bonds between amine or hydroxyl group [1]. Due to acceptor and donor properties both type of compounds are complementary and this fact can be promising in designing and obtaining new cocrystals of amines and alcohols with more complicated motifs and architectures. Using IR laser assisted in situ crystallization technique eleven new crystals was obtained [2]. Most of them crystallize in monoclinic system with 1:1 stoichiometry. All structures exhibit layered architectures consisting of pleated ribbons. The most primitive and repeatable motif in these arrangement is four-membered ring build by two amine and two hydroxyl group with a center of symmetry in the middle. However there are some structure with this motif but with other symmetry element, such us two-fold axis. The structure of pure of dimethyl-1,3-propandiamine has not been described due to formation of this amine the plastic phase in room temperature. Cooling down the sample causes phase transition between disordered F-centered cubic phase and I-centered tetragonal ordered phase. Similar situation is present in cocrystal of this amine with tert-butanol. In order to describe these phenomena's an hydrogen bond dynamics powder diffraction, differential scanning calorimetry and Raman studies were conducted.

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Keywords: diamines, alcohols, cocrystals

MS10-O4

Accurate hydrogen atom positions from standard X-ray Data: hirshfeld atom refinement and olex2

Horst Puschmann1, Oleg Dolomanov1

1. OlexSys Ltd, Chemistry Department, Durham University, Durham, United Kingdom

email: horst.puschmann@gmail.com

"Hirshfeld atom refinement (HAR) is a novel X-ray structure refinement technique that employs aspherical atomic scattering actors obtained from stockholder partitioning of a theoretically determined tailor-made static electron density. HAR overcomes many of the known limitations of independent atom modelling (IAM), such as too short element-hydrogen distances, r(X-H), or too large atomic displacement parameters (ADPs)" [1] HAR is now available in the general release version of Olex2 [2]. Given a standard X-ray dataset of good quality, information that could so far only be obtained by neutron diffraction can now be determined using HAR: accurate hydrogen atom positions. The residual electron density maps derived from this quantum crystallographic technique will also be much 'cleaner' than those obtained from standard Independent Atom Model (IAM) refinements. HAR is easy to run from Olex2, and in this contribution, I will introduce what HAR is, how it is implemented in Olex2 and how you run it. I will also discuss the current limitations of the technique. I invite you to try this at home: this presentation is available online and contains everything you need to know to get started [3]. Olex2 is open-source, available for Windows, MacOS and Linux and is free of charge.



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 https://tinyurl.com/ycrsqzjl

MS10-O5

Joint X-ray and Neutron protein crystallography for the study of enzymeisoform selectivity by small molecule inhibitors

Zoe Fisher¹, Katarina Koruza², Brian Mahon³, Matthew Blakeley⁴, Tobias Schrader⁵, Andreas Ostermann⁶, Wolfgang Knecht⁷, Robert McKenna⁸

- Scientific Activities Division, European Spallation Source, Lund, Sweden
- 2. Biology Department, Lund University, Lund, Sweden
- Department of Molecular Biology, Princeton University, Princeton, United States of America
- 4. Large-Scale Structures Group, Institut Laue-Langevin, Grenoble, France
- Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München, Garching, Germany
- Forschungszentrum Jülich GmbH, Jülich Centre for Neutron Science (JCNS) at Heinz Maier-Leibnitz Zentrum (MLZ), Garching, Germany
- Lund Protein Production Platform & Biology Department, Lund University, Lund, Sweden
- Biochemistry and Molecular Biology Department, University of Florida, Gainesville, United States of America

email: zoe.fisher@esss.se

Human carbonic anhydrase IX (CA IX) expression is actHuman carbonic anhydrase IX (CA IX) expression is activated by hypoxic condition in aggressive, metastatic tumors. Cancer patietns positive for CA IX have generally a poor prognosis. CA IX has emerged as an important cancer target, but efforts to develop isoform selective inhibitors are complicated by the presence of 14 other CA isoforms that share high sequence and structural similarity. This leads to off-target inhibitor binding and side effects. Recent studies showed that saccharin (SAC) already shows some isoform discrimination, and that conjugating SAC to a glucose molecule (Saccharin-Glucose Conjugate, SGC) further improves the Ki against CA IX by 2-fold. Ligand binding to proteins are mediated through numerous interactions, including: H-bonding directly and/or through intervening waters, electrostatic interactions with charged or polar amino acid side chains, metal coordination, energetic changes through water displacement, aromatic ring stacking, or other hydrophobic interactions. As neutrons scatter strongly from atomic nuclei of light atoms 1H (Hydrogen), and its isotope ²H (Deuterium), it is possible to use neutron protein crystallography (NPX) to "see" the light atoms and any interactions they are involved with. (e.g. H-bonds). We used joint X-ray and neutron crystallography methods to determine the crystal structures of a CA IX mimic alone and in complex with SAC and SGC, respectively. Our analyses reveal the molecular details of solvent displacement upon ligand binding, the H-bonding between the ligands and the proteins, involvement of water-mediated H-bonds, and the remodeling of H-bonds to accommodate ligand binding. The structures and analysis also provide an explanation for the observed CA isoform selectivity of the ligand under study.

Keywords: joint neutron and x-ray crystallography, hydrogen bonding

MS11 Hot structures in biology

Chairs: Prof. Maria Joao Romao, Prof. Fred Antson

MS11-01

Structural basis of human mitochondrial transcription

Hauke Hillen1

1.Max-Planck-Institute for Biophysical Chemistry, Department of Molecular Biology, Göttingen, Germany

email: hauke.hillen@mpibpc.mpg.de

Human carbonic anhydrase IX (CA IX) expression is activated by hypoxic condition in aggressive, metastatic tumors. Cancer patietns positive for CA IX have generally a poor prognosis. CA IX has emerged as an important cancer target, but efforts to develop isoform selective inhibitors are complicated by the presence of 14 other CA isoforms that share high sequence and structural similarity. This leads to off-target inhibitor binding and side effects. Recent studies showed that saccharin (SAC) already shows some isoform discrimination, and that conjugating SAC to a glucose molecule (Saccharin-Glucose Conjugate, SGC) further improves the K_i against CA IX by 2-fold. Ligand binding to proteins are mediated through numerous interactions, including: H-bonding directly and/or through intervening waters, electrostatic interactions with charged or polar amino acid side chains, metal coordination, energetic changes through water displacement, aromatic ring stacking, or other hydrophobic interactions. As neutrons scatter strongly from atomic nuclei of light atoms ¹H (Hydrogen), and its isotope ²H (Deuterium), it is possible to use neutron protein crystallography (NPX) to "see" the light atoms and any interactions they are involved with. (e.g. H-bonds). We used joint X-ray and neutron crystallography methods to determine the crystal structures of a CA IX mimic alone and in complex with SAC and SGC, respectively. Our analyses reveal the molecular details of solvent displacement upon ligand binding, the H-bonding between the ligands and the proteins, involvement of water-mediated H-bonds, and the remodeling of H-bonds to accommodate ligand binding. The structures and analysis also provide an explanation for the observed CA isoform selectivity of the ligand under study.

The mitochondrial genome is transcribed by a dedicated mitochondrial RNA polymerase (mtRNAP), which also generates the RNA primers required for DNA replication. Unlike the distantly related bacteriophage RNA polymerases, mtR-NAP requires auxiliary protein factors for each step of the transcription cycle. However, the molecular mechanisms underlying mitochondrial transcription are poorly understood. While the structures of the mitochondrial polymerase and of some mitochondrial transcription factors have been reported, structural data on the interplay between these factors and the polymerase in functional complexes has been lacking. We have determined the structure of the human mitochondrial transcription initiation complex, which reveals how the initiation factors TFAM and TFB2M facilitate promoter binding and DNA opening, respectively. Furthermore, we have solved the structure of the mitochondrial

transcription elongation factor TEFM and of an anti-termination complex consisting of TEFM bound to the transcribing polymerase. These structures illustrate how TEFM interacts with both the nucleic acid and the polymerase in the elongation complex to facilitate processive transcription and drive gene expression over primer formation for DNA replication. Together, these results elucidate the mechanistic basis of transcription initiation and processive elongation in human mitochondria and provide the framework for studying the regulation of mitochondrial gene transcription.

Keywords: Mitochondria, Transcription, RNA

MS11-O2

Structural and functional insight into human O-GlcNAcase

Christian Roth¹, Sherry Chan², Wendy Offen², Lianne Willems³, Dustin King³, Robert Britton³, David Vocadlo³, Gideon Davies¹

- Carbohydrates: Structure and Function, Biomolecular Systems, Max Planck Institute of Colloids and Interfaces, Berlin, Germany
- 2. York Structural Biology Laboratory, Department of Chemistry University of York, York, United Kingdom
- 3. Department of Chemistry, Simon Fraser University, Burnaby, Canada

email: christian.roth@mpikg.mpg.de

O-GlcNAc hydrolase, OGA, removes O-linked N-acetylglucosamine (O-GlcNAc) from myriad nucleocytoplasmic proteins. O-GlcNAcylatation plays a vital role in a range of cellular processes including, for example, transcriptional regulation and the stress response (reviewed in Ref 1,2). Dysregulation of O-GlcNAcylation has been implicated in diseases including cancer3, and neurodegenerative diseases.4,5 Notably, therapeutic agents targeting the O-GlcNAc modification have entered phase I clinical trials against neurodegenerative disorders, stimulating interest in the molecular and chemical basis of O-Glc-NAcylation and its manipulation with small molecules.6 We aimed to shed light on the multi-domain architecture of OGA and the structural basis of activity. Through co-expression and assembly of OGA fragments we determined the 3-D structure of human OGA, revealing an unusual helix exchanged dimer that lays a structural foundation for an improved understanding of substrate recognition and regulation of OGA.7 Structures of OGA in complex with a series of different inhibitors define a precise blueprint for the design of lead structures having potential clinical value.

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Keywords: glycoside hydrolase, neurodegenerative disease, inhibitor design

MS11-O3

Grouper Iridovirus GIV66: a Bcl-2 protein that inhibits apoptosis by exclusively sequestering Bim

Sofia Caria1 ,Suresh Banjara2, Timothy M. Ryan3, Marc Kvansakul2

- 1. La Trobe Institute for Molecular Science, La Trobe University and Australian Synchrotron, ANSTO, Bundoora & Clayton, Australia
- La Trobe Institute for Molecular Science, La Trobe University, Bundoora, Australia
- 3. Australian Synchrotron, ANSTO, Clayton, Australia

email: sofia.caria@synchrotron.org.au

Programmed cell death or apoptosis is a critical mechanism for the controlled removal of damaged or infected cells, and proteins of the Bcl-2 family are important arbiters of this process. Viruses encode functional and structural homologs of Bcl-2 to highjack host cell apoptosis and ensure viral proliferation and/or survival. Grouper iridovirus (GIV) is a large DNA virus belonging to the iridoviridae family that harbors GIV66, a putative Bcl-2 like protein. GIV66 is a mitochondrially localized inhibitor of apoptosis, however the molecular and structural basis of apoptosis inhibition is currently not understood. Our studies show that GIV66 harbors an unusually high level of specificity for pro-apoptotic Bcl-2, and only engages with Bim. We then determined crystal structures of both apoGIV66 as well as bound to Bim BH3. Unexpectedly, apoGIV66 forms dimers via a novel interface that occludes access to the canonical Bcl-2 ligand binding groove, which break apart upon Bim binding. SAXS studies were crucial to further eluciate the mechanism of action of GIV66 in inhibiting apoptosis. GIV66 dimerization seems to impacts on the ability of GIV66 to bind and select host pro-death Bcl-2 protein.

Keywords: viral Bcl-2, SAXS, crystallography,

MS11-04

Crystal structures of bacteriophage receptor binding proteins

Mark Johan van Raaij¹, Marta Sanz-Gaitero², Antonio Pichel-Beleiro², Mateo Seoane-Blanco²

- 1. Departamento de Estructura de Macromoleculas, Centro Nacional de Biotecnologia, CSIC, Madrid, Spain
- 2. ñ CNB-CSIC, Madrid, Spain

email: mjvanraaij@cnb.csic.es

Bacteriophages have specialized receptor binding proteins for initial, reversible, host cell wall recognition. Once a suitable host is found, the phage commits to infection by irreversible attachment via a secondary receptor interaction. The crystal structures of several of these receptor-binding proteins have been solved and have been shown to be mainly beta-structured, but structurally highly diverse and containing several new protein folds. Structures of the receptor-binding proteins of the coliphages T4, T5 and T7, of the Salmonella phage epsilon15 and of the Staphylococcus phages S241 and K will be shown.

Ongoing structural, mutational and binding analysis of virus receptor-binding proteins with receptors and receptor analogues will be discussed. Bacteriophage receptor-recognizing proteins may be used for bacterial detection, while modification by natural or experimental mutation of bacteriophage receptorbinding domains may allow retargeting of phages to alternative host bacteria. Their shape and stability may also allow their use in nanotechnological applications.

Keywords: Antibiotic resistance, bacterial detection, proteinligand interaction

MS11-05

Structural basis for RpoS regulation via ClpXP adaptor/anti-adaptor pairs

Alexandra Deaconescu¹, Victoria Dorich¹, Margaret Suhanovsky², Arti Tripathi³, Song Tong³, Christiane Brugger¹, Joel Hoskins³, Sue Wickner², Susan Gottesman³

- Department of Molecular Biology, Cell Biology and Biochemistry, Brown University, Providence, United States of America
- Department of Molecular Biology, Cell Biology and Biochemistry, Providence, United States of America
- Laboratory of Molecular Biology, National Cancer Institute, Bethesda, United States of America

email: alexandra_deaconescu@brown.edu

The promoter dissociable subunit RpoS is widely recognized as the master regulator of the bacterial stress response. Its intracellular levels are not steady, but fluctuate in response to nutrient starvation or other environmental stress signals such that during the logarithmic phase, RpoS is almost undetectable, while in stationary phase, it rapidly accumulates to enable transcription reprogramming via control of a large regulon. This process is largely controlled at the level of RpoS proteolysis by the ClpXP machinery, which readily occurs under active growth, and is inhibited upon stress. Here we provide mechanistic and structural insights into how RpoS delivery to the ClpXP machine is inhibited by small factors collectively called anti-adaptors. Anti-adaptors are induced by specific stress signals and bind to RssB, a ClpXP adaptor of exquisite specificity that is required for RpoS loading onto ClpXP and represents the limiting factor in this process. Our data suggest that anti-adaptors may utilize modes of RssB recognition that rely heavily of RssB plasticity.

Keywords: RpoS, ClpXP, RssB

MS12 Structural bioinformatics

Chairs: Claudia Lucía Millán Nebot, Dr. Daniel Rigden

MS12-01

Using evolutionary couplings to predict contacts and build structures

Kelly Brock1, Chris Sander2, Debora Marks1

- Department of Systems Biology, Harvard Medical School, Boston, MA, United States of America
- 2. cBio Center, Dana-Farber Cancer Institute + Harvard Medical School, Boston, MA, United States of America

email: kpgbrock@gmail.com

Recent advances in crystallography have helped deliver unparalleled biological insight; however, the rate at which experimental structures can be solved still lags behind the need to better understand many biomolecules. Our research aims to significantly **accelerate** the accumulation of structural knowledge through computational means, including collaborating with experimental labs to help solve and refine models of protein monomers and complexes.

To help bridge the gap between protein sequence and 3D structure, our lab uses a protein's evolutionary history to predict which residues are most likely to physically interact. Identifying potential interacting pairs, or **evolutionary couplings** (ECs), can be achieved by finding related sequences and applying a global probability model to search for covariation patterns consistent with interacting residues. We have shown that ECs can be sufficient to predict the tertiary fold of a protein [1,2], and thousands of pre-computed models along with our web server can be found at **EVcouplings.** org.

We recently helped solve the structure of the 359-residue transmembrane protein RodA by generating a de novo folded model that was sufficient for molecular replacement, and we predicted how it forms a complex with its binding partner PBP2 [3]. We can provide models for unknown component structures in 3D complex determination, along with predictions about protein-protein contacts. Here, we present the potential for ECs to help build and refine models in conjunction with crystallography data.

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resolved by evolutionary coupling analysis. Nature 2018.

Keywords: molecular replacement, contact prediction

MS12-O2

CATH funfams for domain boundary recogniton and template selection

Christine Orengo1, Ian Sillitoe1, Sayoni Das1, Jon Lees1

1. University College London, London, United Kingdom

email: c.orengo@ucl.ac.uk

The CATH domain structure database (www.cathdb.info) classifies domains of known structure from the PDB and predicted domains from sequences in UniProt. The major focus is on identifying evolutionary relatives, which are classified into superfamilies. Superfamilies are subsequently annotated using a hierarchical model, according to their fold group, architecture and protein class (Dawson et al. 2017). Sequence profiles are derived from representatives in each superfamily and Hidden Markov Models (HMMs) generated using HMMer3 (Lees et al. 2017). CATH currently comprises, ~450,000 domain structures and ~90 million domain sequences, classified into ~6000 evolutionary superfamilies. The latest version (CATH 4.2) captures more than 90% of domains identified in the PDB. However more than 50% of the domains are classified in fewer than 200 'mega' superfamilies, which have diverged considerably in the structures and functions of the relatives - although the structural core remains very highly conserved. Detailed analyses have revealed considerable structural diversity outside this core, often in functional regions of the protein eg around active site pockets, where the changes may be associated with modifications in function, particularly for paralogous proteins.

In order to explore the divergence of structure and function within superfamilies, we have developed a sub-classification protocol which groups relatives having highly similar structures and functions into functional families (FunFams). This is achieved using an agglomerative clustering protocol, with functional groupings recognised from distinct differences in patterns of sequence conservation, likely to be associated with functional determinants (Das et al. 2015). CATH-FunFams tend to be highly structurally coherent relatives typically superpose within 2A RMSD. We have developed protocols that use the FunFams to provide improved domain boundary assignment for query sequences and to select suitable templates for homology modelling or structure determination. FunFams were used by the PSI MCSG Structural Genomics Consortium to improve construct generation. FunFams were also used to identify targets likely to have novel functions, for structure determination. They can also be used to facilitate the interpretation of genetic variants linked to disease.

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Keywords: structural bioinformatics, domain boundary identification, functional family classification

MS12-O3

Exploiting residue-residue contact information beyond structure predictions in Molecular Replacement

Felix Simkovic¹, Saulo de Oliveira², Charlotte Deane², Daniel J Rigden¹

- 1. Department of Biochemistry, University of Liverpool, Liverpool, United Kingdom
- 2. Department of Statistics, University of Oxford, Oxford, United Kingdom

email: hlfsimko@liv.ac.uk

Interactions between amino acids are crucial for protein folding and interactions. Natural selection can therefore limit changes to conservative substitutions or simultaneous changes at two positions, leaving a covariance signal between them. Successful detection of these positions, through the analysis of evolutionary covariance, is now reliably possible [1]. Beyond the immediate impact this data has already made in the field of Structural Biology, many applications specifically in X-ray crystallography are yet to be tested or determined [2].

Ab initio protein structure prediction is typically done by assembling protein fragments selected using the target sequence. Here we describe the use of contact information to select protein fragments for direct use as search models. The selection of fragments is supported by matching the target-specific contact profile to a fragment, thus extracting fragments more likely to be similar to the target fold. We show how such fragments can be directly used as Molecular Replacement search models to successfully elucidate the structure of small globular protein targets. The findings are particularly relevant for targets for which conventional Molecular Replacement fails and idealised helices are not sufficient.

Another example of the use of contact information to aid X-ray crystallography is the applicability of residue-residue contacts to select accurate *ab initio* structure predictions. The use of such predictions to generate ensemble search models in the unconventional MR pipeline AMPLE has been described [3]. Here we consider how it may be possible to select and process single favoured structures as an alternative route to structure solution in difficult cases.

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Keywords: ab initio modelling, evolutionary covariation, molecular replacement

MS12-O4

ALEPH: a network-oriented approach to structure mapping and comparisons

Massimo Domenico Sammito¹, Ana Medina², Claudia Millán², Rafael J. Borges³, Isabel Usón⁴

- Department of Haematology, Cambridge Institute for Medical Research, University of Cambridge, Cambridge, United Kingdom
- Crystallographic Methods, Institute of Molecular Biology of Barcelona (IBMB), Spanish National Research Council (CSIC), Barcelona, Spain
- 3. Dept. Physics and Biophysics, Biosciences Institute (IBB), São Paulo State University (UNESP), Botucatu, Brazil
- Structural Biology, Catalan Institution for Research and Advanced Studies (ICREA), Institute of Molecular Biology of Barcelona (IBMB), Spanish National Research Council (CSIC), Barcelona, Spain

email: massimo.sammito@gmail.com

The folding of an amino acid sequence into stable secondary structure fragments represents one of the most energetically favorable and hence initial steps for the formation of tertiary structure in almost all protein families. Therefore, a description based only on these basic structural elements is a powerful abstraction that allows structure comparison and classification. In our group, we define as Local Folds^[1](LF) any characterization of nonspecific, small, discontinuous composites of secondary structure elements. The retrieval of libraries of ubiquitous LF has been possible through specialised software. Such libraries have been used to phase (from crystallographic data) larger and even all-beta structures following an ab-initio approach^[1]. In our group, LF characterization is performed through a new software called ALEPH; it is based only on 3d-geometrical descriptors named Characteristic Vectors^[1] whose relations are described with a network. Interpretation of this network results in a specific signature for every structure. Structure comparisons through signatures do not require sequence alignments and allow to abstract folds, domain, and even LF without performing superpositions or coordinate-based algorithms. This generalization can be used also for the generation of structural ensembles for Molecular Replacement (MR) or to automatically determine compact secondary structure subgroups to apply new Phaser Gyre/ Gimble^[2] functions for solution optimization as recently reported in ARCIMBOLDO SHREDDER^[3]. The nature of the problem requires data mining over more than 130,000 structures deposited in the Protein Data Bank and the design of specialized algorithms to build, inspect and compare CV networks.

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Keywords: Structure comparison, Local Folds, Network analysis

MS12-O5

Validation and quality assessment of macromolecular structures using complex network analysis

Jure Pražnikar¹, Miloš Tomić², Dušan Turk³

- Institut Jožef Stefan Ljubljana; Faculty of Mathematics, Natural Sciences and Information Technologies - University of Primorska, Ljubljana & Koper, Slovenia
- 2. Faculty of Mathematics, Natural Sciences and Information Technologies, University of Primorska, Koper, Slovenia
- 3. Institute Jožef Stefan, Ljubljana, Slovenia

email: jure.praznikar@upr.si

Validation of three-dimensional structures is at the core of structural determination methods. The local validation criteria, such as deviations from ideal bond length and bonding angles, Ramachandran plot outliers and clashing contacts, are a standard part of structure analysis before structure deposition, whereas the global and regional packing may not yet have been addressed. In the last two decades, three-dimensional models of macromolecules such as proteins have been successfully described by a network of nodes and edges. Amino acid residues as nodes and close contact between the residues as edges have been used to explore basic network properties, to study protein folding and stability and to predict catalytic sites. Using complex network analysis, we introduced common network parameters to distinguish between correct and incorrect three-dimensional protein structures. The analysis showed that correct structures have a higher average node degree, higher graph energy, and lower shortest path length than their incorrect counterparts. Thus, correct protein models are more densely intra-connected, and in turn, the transfer of information between nodes/amino acids is more efficient. Moreover, protein graph spectra were used to investigate model bias in protein structure.

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Keywords: macromolecule, structure validation, complex network MS13 New insights on diffraction studies of minerals and related materials

> Chairs: Dr. Catherine Dejoie, Prof. Giuseppe Cruciani

MS13-01

Insights into water-rock interactions in meteorites from diffraction tomography

Agnès Elmaleh¹, Jonathan P. Wright², Benoît Baptiste¹, Serena C. Tarantino³, Béatrice Doisneau¹, Erik Elkaim⁴, David Troadec⁵

- 1. Inst. de Minéralogie de Physique des Matériaux et de Cosmochimie, Sorbonne Université / CNRS, Paris, France
- 2. European Synchrotron Radiation Facility, Grenoble, France
- Dip. di Scienze della Terra e dell'Ambiente, Universitá degli studi di Pavia, Pavia, Italy
- 4. Synchrotron Soleil, Gif-sur-Yvette, France
- Inst. d'Électronique de Microélectronique et de Nanotechnologie, Université de Lille / CNRS, Villeneuve d'Ascq, France

email: agnes.elmaleh@upmc.fr

Mineral hydration reactions occurred in small bodies of the solar system, likely at early stages of its history through the melting of ices accreted together with rocks, in areas located beyond the snowline. Carbonaceous chondrites, which are primitive meteorites, are witnesses of these reactions and mostly consist of hydroxylated layered silicates [1]. Their study provides understanding of the nature and stability of minerals that are important carriers of water across the solar system, and of the conditions of their formation. In carbonaceous chondrites, minerals formed during water-rock interactions present a large range of sizes (from several microns down to a few nanometers) and of compositions. In particular, the diversity of the compositions of layered silicates, mostly serpentines, exceeds by far that of terrestrial ones, including Fe and Al-rich end members; characterizing their structure is challenging because of their sub-micron size, heterogeneity and order-disorder pattern [2]. We will present results obtained by synchrotron X-Ray Diffraction Computed Tomography (XRD-CT [3]) on a series of carbonaceous chondrites of the CM family, which are carbon and hydrogen-rich chondrites in which the relatively good preservation of primary minerals allows for the reactions of hydration to be studied. We will show that varying the size of the focused beam down to 100 nm and in combination with absorption tomography, it is possible to map the distribution of hydrated nanometer-sized minerals that are difficult to characterize even by TEM, to highlight their relationship to primary anhydrous phases, and to obtain high resolution powder XRD patterns and single crystal XRD data of serpentines. Finally, we will show preliminary results of the integration of structural data and crystal-chemistry (composition, Fe valence state) of chondritic serpentines, aiming at better understanding their mixing properties along the Fe2+-Fe3+-Al3+-Mg2+ solid solutions.

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Keywords: synchrotron, XRD, carbonaceous chondrites

MS13-O2

Synchrotron X ray powder diffraction for the study of cutting edge zeolites applications

Lara Gigli¹

1. Elettra-Sincrotrone Trieste, Basovizza, Trieste, Italy

email: lara.gigli@elettra.eu

Among the tectosilicates family, zeolites - of natural and synthetic origin - are certainly one of the most interesting one. Thanks to their peculiar microporous structure and chemistry, they have been widely used as highly efficient catalysts, adsorbents, and ion exchangers in petrochemical industries and in our daily life [1]. Beyond these traditional applications, recently zeolites are playing an increasingly important role in diverse areas, ranging from the environmental protection [2] to the advanced technological fields [3]. In particular, zeolites have found promising applications in the fields of renewable energy and environmental remediation, such as solar energy transport, thermal energy storage, CO₂ capture and water, soil treatment, etc. These applications make zeolites potential candidates as solutions to the sustainability issues in our society. This contribution will review some recent studies on the development of hybrid supramolecular structure (dyes/zeolite) suitable in Förster resonance energy transfer sensitized solar cell and luminescent solar concentrators and the use of high silica zeolites as adsorbent of emerging organic contaminant (ECOs) such as pharmaceutical active compounds and pesticides. Synchrotron X ray powder diffraction combined with other experimental techniques (infrared, UV-vis spectroscopy and liquid chromatography, etc.) and theoretical modeling-can be efficiently exploited to realistically localize the guest molecules in the zeolite pores. This multidisciplinary approach is of fundamental importance for the interpretation of the host -guest interaction at the base of the molecular organization and adsorption mechanisms.

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Keywords: synchrotron, XRD, zeolites

MS13-O3

Cation migrations and Bronsted sites formation in NH₄-form of zeolite omega: a combined in situ time-resolved Synchrotron and Neutron powder diffraction study

Giada Beltrami¹, Annalisa Martucci¹, Francesco Di Renzo², Alberto Alberti¹, Maria de Lourdes Guzman-Castillo³, Francois Fajula²

- 1. Dept. of physics and Earth Sciences, University of Ferrara, Ferrara, Italy
- Institut Charles Gerhardt, UMR 5618 UM-CNRS-ENSCM, ENSCM, Montpellier, France
- 3. Istituto Mexicano del Petroleo, Mexico D.F., Mexico

email: bltgdi@unife.it

Acidic zeolites are usually exploited by petroleum industries as high-performing catalysts. Thus far, they have been successfully employed with different purposes, such as isomerization of xylenes, paraffin hydro- isomerization, catalytic cracking, and heavy oil hydrocracking [1]. Their catalytic properties arises from the presence of protons bonded to framework oxygen atoms, which act as Brønsted acid sites. To predict the zeolite performances as acid catalysts, a detailed structural study is needed in order to determine location, nature, strength and density of acid sites. Based on this, the aim of this work is to give an exhaustive picture of thermal behaviour of zeolite omega (a synthetic counterpart of the natural mazzite zeolite) [2] in its NH4-form, from RT to 900 °C in order to follow the structural modifications induced by calcinations of ammonium ions. The formation of Brønsted sites was also monitored by neutron diffraction in order to detect their location. A sample of zeolite omega (Na6.6TMA1.8(H2O)22.2[Al8.4Si27.6O72]-MAZ) was synthetized at the Laboratoire de Matèriaux Catalytiques et Catalyse en Chimie Organique, (CNRS, Montpellier, France) and then NH4-ion exchanged three times at Room Temperature and other three times at 90 °C (Na2.4T-MA0.9(H2O)4.2(NH4)20.0[Al8.4Si27.6O72]). The "in-situ" time resolved diffraction measurements were performed at ESFR, Grenoble (heating rate was 5°C/min). The loss of extraframework species (residual TMA and NH4) was accompanied by strong deformation to the zeolite framework (i.e., variation on O-O distances and T-O-T angles for 6MR, 8MR and gmelinite cage) and by Na cations migration towards the 6MR. The decrease in T-O2-T angle causes a shift of O2 framework oxygen towards the centre of gmelinite cage, as proved by the decrease of O1-O2 distance addressed by the formation of a O2-H Brønsted acid site, whose location was highlighted by neutron powder data collected at the diffraction beamline D2B (ILL Grenoble). The neutron structure refinement showed that the mean T-O distances are consistent with Si, Al disorder, showing that the small difference (0.015 Å) indicate that more Al is in T2 (or A) than in T1 (or B) in agreement with the results obtained from single crystal X-ray refinement of natural mazzite [3]. Above 770 °C, the strongly inhomogeneous lengthening of the T-O5 distance indicates that a dealumination process occurs. All these informations provide a basis for the interpretation of the omega shape selectivity in reactions of growing importance in the oil and petrochemical industries.

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Keywords: acid, omega, diffraction

MS13-O4

The system Na₂O-CaO-SiO₂: 90 years of research, but do we really know everything?

Volker Kahlenberg1, Daniela Schmidmair1

1. Institute of Mineralogy and Petrography, University of Innsbruck, Innsbruck, Austria

email: volker.kahlenberg@uibk.ac.at

In their landmark paper from 1925 Morey & Bowen [1] presented the first comprehensive description of the phase relationships and melting behavior of the compounds belonging to the ternary system Na₂O-CaO-SiO₂. Due to its fundamental importance for many fields of industrial inorganic chemistry and technical mineralogy this system has been in the focus of a large number of subsequent studies dealing with both basic and applied aspects of silicate science. After more than 90 years of research activities one should assume that no problems remain to be solved.

In the course of an ongoing project on the high-temperature chemistry of compounds in the systems M₂O-RO-SiO₂ (M: Na, K; R: Ca, Sr, Ba) we realized that even for the most intensively studied Na-Ca-silicates suspicion has to be attached not only to what concerns their melting characteristics but also to what concerns the number of existing phases. Despite the compounds whose existence has been unequivocally proofed by a combination of chemical analysis and crystal structure determination there is still a large number of phases mentioned in the literature which, at best, have been characterized by unindexed powder diffraction patterns. Furthermore, in many cases even the compositions have not been thoroughly studied after synthesis. This information, however, is definitely of great importance when dealing with volatile components such as Na₂O or K.O at temperatures above 1000°C.

We were able to demonstrate that Na₂Ca₆Si₄O₁₅, for example, which has been first synthesized via hydrothermal methods [2] can be also obtained under dry conditions using Na₂CO₃, CaCO₃ and SiO₂ as educts. Therefore, the ternary phase diagram, where this compound has not been taken into consideration, has to be revised. In-situ hightemperature powder diffraction experiments were used to determine the thermal expansion tensor of Na₂Ca₈Si₄O₁₅ between ambient temperature and 1100°C. Furthermore, the crystal structure of a new high-temperature polymorph of the compound has been determined. Finally, comprehensive synthesis experiments using solid state reactions as well as re-crystallization studies from glasses revealed that several previously described sodium calcium silicates such as Na₈Ca₅Si₅O₁₇, Na₂Ca₅Si₀O₈ and Na₂CaSi₅O₁₂ could not be reproduced indicating that a question mark has to be put on their existence.

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Keywords: Ternary system, Na₂O-CaO-SiO₂, phase relationships

MS13-05

Structural resolution of inorganic nanotubes with complex stoichiometry

Geoffrey Monet¹, Mohamed Salah Amara¹, Stéphan Rouzière¹, Erwan Paineau¹, Pascale Launois¹

1. Laboratory of Solid State Physics, Orsay, France

email: monet_geoffrey@hotmail.fr

Determination of the atomic structure of inorganic single-walled nanotubes with complex stoichiometry remains elusive due to the too many atomic coordinates to be fitted with respect to X-ray diffractograms inherently exhibiting rather broad features. Here we introduce a new approach which enables resolution of their structure [1]. It is based, first, on the use of helical symmetries allowing one to consider the smallest unit cell and then on semi-empirical energy minimization leading to a reduction of the number of structural parameters to be fitted. We applied this method to recently synthesized methylated alumino-silicate and alumino-germanate imogolite nanotubes of nominal composition (OH)3Al2O3Si(Ge) CH₃ [2]. Imogolite (OH)₃Al₂O₃Si(OH) is a clay mineral present in soils, also synthesized by soft chemistry. Thanks to their chemical versatility, imogolite-like nanotubes (INT) are promising candidates for applications in molecular storage, recognition and separation [3]. Fit of wide-angle X-ray scattering (WAXS) diagrams of methylated INTs enabled us to determine their atomic structure. We show that unlike their (N,0) zigzag hydroxylated analogs (OH)₃Al₂O₃Si(Ge)OH, methylated imogolite nanotubes roll up into a (N.N) armchair structure. (Figure). The transferability of the approach opens up for improved understanding of structure-property relationships of inorganic nanotubes, including minerals nanotubes, to the benefit of fundamental and applicative research in these systems.



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Keywords: Metal-oxide nanotube, Imogolite, WAXS

MS14 Combined approaches for structure characterization of modulated and complex structures

Chairs: Prof. Joke Hadermann, Dr. Phillipe Boullay

MS14-01

Investigation of the structure of the modulated doubly ordered perovskite NaLaCoWO₆ and its reversible phase transition with a colossal temperature hysteresis

Claire V. Colin¹, Peng Zuo¹, Céline Darie¹, Holger Klein¹

1. Institut Néel, CNRS & Université Grenoble Alpes, Grenoble, France

email: claire.colin@neel.cnrs.fr

Magneto-electric multiferroics are drawing considerable research interests not only for the variety of attractive fundamental phenomena but also for potential technological applications such as energy efficient memory devices and multiple state memories. To overcome the shortcomings of known multiferroics, a new approach to inducing spontaneous ferroelectric polarization by a combination of two non-polar rotation modes of the oxygen octahedra in magnetic materials was proposed. This so called "Hybrid Improper Ferroelectricity (HIF)"1 could lead to materials exhibiting high polar fields and a strong coupling with magnetism, making them promising for applications. In the framework of research for more materials displaying HIF experimentally, we have investigated NaLnCoWO₆ compounds with Ln= lanthanides.2 Synchrotron X-ray powder diffraction and neutron powder diffraction have shown that all compounds have layered Na/Ln ordering and rocksalt Co/W ordering, and nine compounds (Ln = Y, Sm-Yb) crystallize in the polar $P2_1$ space group. The structure is indeed the targeted one of a doubly ordered perovskite. The compound NaLaCoWO6 shows however an unusual behavior. At room temperature, transmission electron microscopy evidences a modulated structure that can be attributed to tilt twinning domains of oxygen octahedra. The modulation disappears at a phase transition at low temperature, where the local structure changes symmetry from the $P2_1/m$ to the polar P21 space group. Neutron powder diffraction reveals, and electron diffraction confirms, an unusually large temperature hysteresis, where the transition takes place at ~180 K on cooling and at ~320 K on heating. The origin of this unusually large hysteresis (140K) will be discussed, in particular the role of the oxygen octahedra tilting modes3.



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Keywords: modulated structure, TEM, neutron powder diffraction, doubly ordered perovskite

MS14-O2

Crystallography at the order-disorder borderline: characterization of nanodomains by electron diffraction and imaging

Enrico Mugnaioli¹, Mauro Gemmi¹, Ira V. Rozhdestvenskaya², Michael Czank³, Wulf Depmeier³, Jeremy David⁴, Giovanni Bertoni⁵, Luca De Trizio⁶, Liberato Manna⁶

- Center for Nanotechnology Innovation@NEST, Istituto Italiano di Tecnologia (IIT), Pisa, Italy
- Department of Crystallography, Institute of Earth Science, Saint Petersburg State University, Saint Petersburg, Russia
- 3. Institute of Geosciences, Kiel University, Kiel, Germany
- Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB, Barcelona, Spain
- 5. IMEM-CNR, Parma, Italy
- Department of Nanochemstry, Istituto Italiano di Tecnologia (IIT), Genova, Italy

email: enrico.mugnaioli@iit.it

Properties of functional nanomaterials strongly depend on their atomic structures and the more or less ordered arrangement of vacancies and defects. Yet, structure characterization by X-ray powder diffraction (XRPD) often suffers from systematic and random peak overlap. Difficulties are drastically enhanced when materials are modulated, with strong discrepancies between sub-cell and satellite reflection intensities, and/or consist of multiple structurally related polytypes. In the last years, electron diffraction tomography (EDT) emerged as an effective method for addressing the atomic structure of natural and synthetic phases available only as sub-micrometric crystals [1]. This method allows collecting 3D diffraction data from coherent regions of few nanometers, also in materials that may just look disordered for standard X-ray diffraction experiments. Anyway, EDT alone may fall short in the characterization of phases where modulations, twinning or stacking faults play a key role and cannot be neglected for a proper understanding of material properties. In this contribution, we present the structure characterization of the highly disordered mineral denisovite and of the modulated plasmonic Cu2-xTe pseudo-cubic nanocrystals, which we eventually achieved combining EDT with high-resolution HAADF-STEM imaging, XRPD and nano-resolved EDX chemical spectroscopies. Denisovite is a nanocrystalline, polytypic, disordered and very complex mineral. Its structure, or, even, the ordered portion of it, ranks among the 1% most complex mineral structures know to date. Additionally, stacking faults and twinning may occur several times within areas consisting of few unit cell repetitions. Coupling EDT data obtained on mostly ordered regions and high-resolution imaging, we could eventually obtain a rather complete description of the denisovite structure and explain it in terms of order-disorder (OD) theory [2]. $Cu_{2x}Te (x \sim 0.5)$ nanocrystals recently attracted a considerable attention for their localized surface plasmon resonance in the near-infrared region. The plasmonic response originates from the presence of Cu vacancies, which lead to the formation of free charges in the valence band of the material. Such vacancies were found to form an ordered arrangement, which results in x3 and x4 modulations in the otherwise pseudo-cubic crystalline structure. A first description of vacancy arrangement was recently proposed [3]. We have pushed forward such investigation coupling nano-beam precession-assisted EDT with nano-resolved STEM imaging and EDX mapping. Low density regions connected with Cu vacancies were localized and correlated with a pseudo-tetragonal twinning, which occurs already for particles of few nanometers

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Keywords: electron diffraction, HAADF-STEM, modulated structures

MS14-O3

Ice-like disorder and phase transitions in cadmium cyanide

Chloe Coates¹, Mia Baise², Arkadiy Simonov³, Josh Makepeace¹, Andrew Seel¹, Ben Slater², Andrew Goodwin¹

- 1. Inorganic Chemistry Laboratory, University of Oxford, Oxford, United Kingdom
- 2. Department of Chemistry, University College London, London, United Kingdom
- 3. Institute for Crystallography and Material Sciences, University of Freiburg, Freiburg, Germany

email: chloe.coates@chem.ox.ac.uk

Materials with strongly correlated disorder can be challenging to characterize crystallographically and are thus often poorly understood despite increasing evidence of the link between local deviations from the average structure and advanced material function. $Cd(CN)_2$ has attracted considerable interest for its very strong isotropic negative thermal expansion (NTE). On average, it adopts the interpenetrated diamondoid structure of cubic ice-VII, a topology is able to host a variety of unexpected phenomena, from the two-intwo-out ice rules proton that govern proton disorder in water ice, to magnetic monopoles and loop states in spin-ices.¹

The correlated disorder in Cd(CN)₂ has its signature in the highly structured diffuse scattering, which (unusually) increases in intensity down to a phase transition at 150 K. There exist two types of disorder in Cd(CN)₂. ¹¹²Cd NMR has shown that the Cd environment favours the two-intwo-out configuration of cyanides which mimics the proton disorder in ice.² This static disorder of the CN groups is intrinsically related to an off-centering of the Cd of up to ~1 Å along the <100> directions.³

Our interest is in understanding the possible role played by disorder in the NTE of this material. Key indications for the existence of such a link come from comparing the behaviour of $Zn(CN)_2$ and $Cd(CN)_2$; the former is substantially less disordered, and also shows much weaker NTE. Moreover, previous DFT studies of ordered Cd(CN)₂ variants fail to predict accurately its elastic properties, and entirely miss the instability responsible for its 150 K phase transition.

Using a combination of X-ray and neutron powder, single-crystal and total scattering diffraction data, alongside DFT calculations and ¹¹³Cd NMR; I will explore the icerules disorder in Cd(CN)₂ and its implications for the microscopic mechanism of NTE. In addition I will present the low temperature structure of Cd(CN)₂ and characterise the phase transition in terms of the soft mode responsible for the NTE. Finally, we show that Cd(CN)₂ can be considered a dipolar equivalent of a defective spin-ice state capable of hosting monopolar excitations.

References:

Keywords: disorder, ice, diffuse

MS14-O4

Al/Si ordering in mullite

Paul Benjamin Klar¹, Iñigo Etxebarria², Gotzon Madariaga¹

- Dpto de Física de la Materia Condensada, Universidad del País Vasco UPV/EHU, Bilbao, Spain
- Dpto de Física Aplicada II, Universidad del País Vasco UPV/EHU, Bilbao, Spain

email: paulbenjamin.klar@ehu.eus

The average crystal structure of mullite (Al4+2xSi2-2xO10-x) is not easy to interpret in terms of the distribution of vacancies and Al/Si on the tetrahedral sites. Satellite reflections and diffuse scattering must be investigated to understand the ordering phenomena in the structure. From the reflection conditions of satellite reflections and the corresponding superspace group, the ideal distribution pattern of vacancies and tetrahedra can be directly derived. However, little is known about the distribution of Si within these tetrahedra, especially with respect to surrounding vacancies. Different NMR and neutron diffraction studies could not give a clear answer [1]. We apply density function theory (DFT) to investigate the Al/Si ordering in mullite. As DFT is not feasible with large structures, incommensurately modulated structures are not suitable and commensurate cases or approximations must be used. For this study, commensurate cases with up to 346 atoms in the composition range $0.2 \le x \le 0.5$ were generated from a superspace model with full vacancy ordering [2]. For each composition, symmetry compliant permutations of Al/Si distributions were analyzed with force-field methods (GULP package [3]). The energetically most stable permutation of each composition was then determined with DFT calculations (VASP) and integrated into the initial superspace model for comparison. The Al/Si ordering for x > 1/3 is defined by one unified superspace model (see Figure below) with Si present in triclusters. A second unified model without Si in triclusters for x < 1/3requires the rotation of certain AlSiO7 diclusters with respect to the first model. Si2O7 diclusters are always sandwiched between two vacancies for the analyzed solid solution range. Structure model refinements in (3+1)d superspace based on synchrotron single crystal X-ray diffraction measurements of mullite with $x \approx 0.4$ cannot distinguish between Al and Si, but the Al/Si ordering can be estimated from the modulated volumes of the tetrahedra. The refined models, which is not fully ordered as only 1st order harmonic functions are used to describe the modulations, agree qualitatively with the predictions from the DFT calculations, i.e. larger volumes are observed where Al is predicted, and smaller volumes where Si is predicted. The unified superspace models derived from DFT are considered to represent the ideal, most ordered state of mullite, from which the not fully ordered real structure can be derived. Financial support by FEDER (No. MAT2015-66441-P) and the Basque Government (project No. IT-779-13, PhD grant) is highly appreciated.

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Figure 1: DFT relaxed models of mullite with x = 0.429 (upper left) and x = 0.5 (bottom left), and the common superspace model.



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Keywords: superspace, density functional theory, Al/Si ordering

MS14-05

Nanocluster model and its application for crystal structure prediction of complex intermetallics

Tatiana Akhmetshina¹, Pavlo Solokha², Roman Eremin¹, Vladislav Blatov¹, Davide Proserpio², Serena De Negri², Adriana Saccone²

1. Samara University, Samara, Russia

2. Università degli studi di Genova, Genova, Italy

email: akhmetshina.tanya@yandex.ru

One of the important thing to know about intermetallics is what they consist of and how building units connection is related to their structure and properties. An automatic procedure of representation of crystal structures as assembling of primary nanoclusters was developed and implemented into the ToposPro program package [1]. This approach is especially efficient to elucidate complex intermetallic structures. Thus, a collection of Topological Types of Nanoclusters (TTN) was created, which can be used for generating topological models of new intermetallics [2]. Further, the robustness of the obtained models can then be proved by quantum-mechanical calculations. In this work theoretical and experimental studies were successfully combined. Using the Nanoclustering procedure we found a group of intermetallics containing icosahedra and icosahedron-based two-shell Mackay clusters as primary building units. Among these the family of compounds belonging to Sc₅₇Rh₁₃ structure type (SG Pm-3) [3] seems to be incomplete since isostructural compounds are reported only for Sc-T systems where T = Rh. Ir. Ru. Pt. It is worth to note that one more structural type with stoichiometry 54:17 similarly composed from icosahedra and Mackay clusters arranged in the bcc mode (SG Immm) exists. Both cited structures can be considered as derivatives from an "ideal" cubic phase with 60:13 stoichiometry [3]. According to our DFT modeling and taking into account thermodynamics aspects, an intermediate phase of orthorhombic symmetry containing Mackay clusters of Pd@Sc12@Sc30Pd12 composition should exist. The Sc-Pd system was studied long ago, but only an approximate composition ~Sc4Pd with no structural data was reported for the Sc-richest phase. Single crystals suitable for X-Ray investigation were mechanically extracted from the arc-melted alloys after the appropriate thermal treatment. Some disorder affects this orthorhombic structure of ~Sc56Pd15 composition, but Mackay clusters do not suffer from it. It is worth noting that new structure is quite unusual: the TTN collection includes merely 60 intermetallic compounds containing Mackay clusters as building units. The obtained results motivate us to continue a deeper exploration of related binary/ternary systems.

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Keywords: intermetallics, nanoclusters, structure prediction

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MS15 Crystallography in Earth and space

Chairs: Dr. Anna Pakhomova, Prof. JuanMa García-Ruiz

MS15-01

Crystallography applied to the earth's lower mantle

Tiziana Boffa Ballaran¹

 Bayerisches Geoinstitut, University of Bayreuth, Bayreuth, Germany

email: tiziana.boffa-ballaran@uni-bayreuth.de

Crystal-chemistry studies have been essential in understanding the physical and chemical properties of minerals and their influence on the dynamic evolution of our planet. The use of diamond anvil cells coupled with X-ray sources has been an excellent tool to allows the structural characterization of new high-pressure phases and to help constraining the structural variations of these materials as a function of composition, pressure and temperature in order to shed light on the chemistry and structure of the deep Earth's. Silicate and oxide minerals, in particular, have been the focus of several studies in Geosciences, because of their abundance in the Earth's interior. Silicates transform with increasing pressure to denser phases having Si in 6-fold coordination and relatively simple structures (i.e. rutile-type, perovskite-type etc.), which have however significantly different properties depending on the extent of their cation substitution. The high-pressure high-temperature behavior of oxide minerals, on the contrary, appears very complex and it is characterized by a large and increasing number of new compounds. This variety of phases may contributes to the seismic observations so far obtained for the Earth's interior, therefore results on the structure-properties relationship of relevant minerals of the Earth's lower mantle will be discussed.

Keywords: high-pressure, Earth's mantle

MS15-O2

Mars mineralogy: The EXOMARS 2020 approach

Fernando Rull¹

1. Fisica Materia Condensada, Cristalografia y Mineralogia, Facultad de Ciencias, Universidad de Valladolid, Valladolid, Spain

email: rull@fmc.uva.es

The Exomars program consists in two missions [1]. The first one, launched in 2016 is based on an orbiter carrying a Trace Gas Orbiter analyzer which is devoted to observe methane and other traces of gas present in the Martian atmosphere or emitted by the surface. The second, to be launched in 2020 consist in a rover carrying a drill capable to collect samples at the surface and below the surface down to 2 meters depth. The rover also contains at the interior an instrumental suite located inside the Analytical Laboratory Drawer (ALD) consisting in three instruments: 1- MicrOmega, an infrared spectrometer mainly devoted to the mineralogical analysis of the samples; 2- RLS, a Raman spectrometer also devoted to the mineralogical analysis and the organic detection on these samples and MOMA (Mars Organic Molecule Analyzer) devoted to identify organic molecules and potential biomarkers. These instruments will analyze the samples at the micro scale under the form of fine powder. Here interest is devoted on the Raman instrument and the role it will play inside the mission. The Raman effect is based on the inelastic light scattering process by the matter when illuminated by a laser. This extremely week effect contains information about the atomic and molecular vibrations of the illuminated material. Among the great advantages of the technique it is worth to mention the non destructive character of the analysis, not needs of physical contact and no sample preparation. In this work the technical development of the instrument to achieve a qualified flight-model will be described. Also, the mineralogical and astrobiological scientific objectives it will address in the framework of the mission objectives and the potential and capabilities it can offer during the operation along the mission on Mars. These capabilities will be illustrated on the basis of a wide experimental analysis at the laboratory and at the field, using in this last case potential terrestrial analogues to Mars.

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[1]- http://exploration.esa.int/mars/46048-programme-overview/ Keywords: Mars Mineralogy; Exomars Mission, Raman Spectroscopy

Keywords: Mars Mineralogy; Exomars Mission, Raman Spectroscopy

MS15-O3

Crystallographic characterization and 3D modeling of synthetic plagioclases: a better understanding of morphologies, connectivity and size distribution depending on temperature.

Claire Charles¹, Elsa Ottavi-Pupier¹, Julien Duquennoy¹, Michihiko Nakamura², Satoshi Okumura², Akira Tsuchiyama³, Kentaro Uesugi⁴, Masayuki Uesugi⁵

- 1. Geosciences Department Institut Polytechnique UniLaSalle, Beauvais, France
- 2. Department of Earth Science, Tohoku University, Tohoku, Japan
- Department of Geology and Mineralogy, Kyoto University, Kyoto, Japan
- 4. Spring-8/JASRI, Koto, Japan
- 5. JSPEC/JAXA, Tsukuba, Japan

email: claire.charles21@gmail.com

Experimental samples of basaltic composition, at different temperatures, were created in laboratory. Synthetic basalt was obtained by cooling control (rate 1°C/h) until 40% of crystallization [1]. In-situ observations of plagioclase crystals were made using X-ray micro-tomography beam lines at SPring-8. Grey levels between glass and plagioclases are close and lots of plagioclases are connected, complicating the automatic image treatment. Moreover using usual software for CT treatment, the images are processed automatically but this method generates problems like the data suppression and the calculation approximations (volume, connectivity, size...).

During this study, three dimensions plagioclase crystals resulting from the experimental samples were designed. The 3D reconstruction has been conducted using the numerical platform 3DEXPERIENCE© developed by Dassault Systèmes (DS). The modeling is carried out manually by working on successive images of the samples in order to observe all the crystals and to consider how they are spatially organized. Thus, sections of crystals have been drawn and linked together to build the crystal shape in 3D.

As the result, all the experimental samples were modeled. The 3D reconstructions (figure) allowed to visualize the textures and the interactions between crystals depending on the temperatures. This has permitted to determine the connectivity and the crystallinity of the samples. Moreover, size measurements on axes and volume measurements of each modeled crystal were performed. The plagioclase 3D Crystal Size Distributions (CSD) with the major axis data and with the minor axis data were calculated. The CSD law expresses the number of crystals per interval size per unit volume [2]. This physical law is aimed at connecting size, distribution and abundance of crystals in a rock to the thermal history. CSD of this study are compared with calculated CSD from previous experimental studies using others methods: 2D modeling and 3D mathematic conversions [1] or 3D modeling with different software and automatic axis calculations [3]. The results show similar curves with: a decrease in the CSD according to the temperature and comparable slopes.

The numerical platform 3DEXPERIENCE© provides many advantages for crystallographic studies, calculation and vi-

sualization. All this work on the physical parameters of the plagioclases has enabled to understand their evolution depending on the temperatures.

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Keywords: "3D modelin" "characterization" "crystals"

MS15-04

Natural phosphides as indicators of planetary systems evolution

Sergey Britvin¹, Michail Murashko², Maria Krzhizhanovskaya¹, Yevgeny Vapnik³, Sergey Krivovichev⁴

- Department of Crystallography, Institute of Earth Sciences, Saint-Petersburg State University, Saint-Petersburg, Russia
- 2. Saint-Petersburg State University, Saint-Petersburg, Russia
- 3. Ben-Gurion University of the Negev, Beer-Sheva, Israel
- Kola Science Center, Russian Academy of Sciences, Apatity, Murmansk Region, Russia

email: sbritvin@gmail.com

Natural phosphides is a specific class of minerals containing phosphorus in a redox state lower than zero. The occurrence of phosphide minerals always indicate on highly reducing geo- or cosmochemical environment. At the same time, phase transformations of phosphides are the sensitive indicators of *P*-*T* conditions occurred during planetary systems formation.^{1,2} Phosphides are the common constituents of meteorites; however, till now they were virtually unknown on the Earth. Our recent findings demonstrate that phosphide minerals could play an essential role at the early stages of the Earth's history, in Archean era.³ We herein summarize the results of the recent studies of natural phosphides, with the emphasis on cosmochemically important system Fe-Ni-P, and provide the insights on the role of these minerals in planetary systems evolution.

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Keywords: phosphide, planetary system, mineral

MS15-05

In-situ studies of clathrate hydrates on icy solar system bodies

Sarah Day¹, Emmal Saf², Stephen P Thompson¹, Aneurin Evans³, Claire Murray¹, Julia Parker¹

- 1. Diamond Light Source, Didcot, United Kingdom
- 2. Newcastle University, Newcastle, United Kingdom
- 3. Keele University, Newcastle-Under-Lyme, United Kingdom

email: sarah.day@diamond.ac.uk

Clathrate hydrates are compound structures consisting of water ice, in which water molecules form cage structures capable of trapping a variety of gas molecules. There is considerable evidence to suggest that clathrate hydrates are present on a number of bodies in the Solar System, playing important roles in their atmospheric evolution and surface processes. For example, the origin of the energetic plumes seen emanating from the south pole of Saturn's moon, Enceladus, by Cassini has been associated with the dissociation of large quantities of clathrates hydrates [1]. This is due to the fact that the plumes have been found to contain gases such as CH₄ and N₂, both of which have poor solubility in liquid water On Mars, clathrates have been postulated to play an important role in the distribution and total inventory of Martian volatiles, including methane and noble gases (Xe, Ar, Kr), and that the dissociation of extensive sub-surface clathrate deposits could be responsible for some of the geomorphological features observed on the surface of the planet [2]. They have similarly been suggested as a mode of depletion for the noble gases in the atmosphere of Titan and as the source of the nitrogen depletion observed in comets. Additionally, clathrates are also of terrestrial importance, being recognised as potentially important materials for future energy recovery and storage, as well as CO₂ sequestration. Clathrates are, however, notoriously unstable, existing only in specific temperature and pressure regimes that depend on the size of the trapped gas molecules, and the structure of the ice cages themselves. While a number of thermodynamic models exist to describe their behaviour, experimental data to support these are lacking, especially in the case of real world systems in which clathrates are forming in environments other than pure water, such as saline oceans

In order to improve our understanding of the structural properties of clathrates and their contribution to the shaping and evolution of these bodies we have conducted in-situ synchrotron X-Ray powder diffraction measurements, in conjunction with Raman spectroscopy and small-angle scattering, at Diamond Light Source, UK. The properties of CO_2 and CH_4 clathrates forming in a variety of saline solutions, over a range of temperature and pressure conditions, analogous to those found on Enceladus, Europa, Mars and Titan have been studied. Details of the experimental setup used and the results of these studies will be presented here.

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Keywords: Clathrates, X-Ray Diffraction, Solar System

MS16 Understanding of functional materials

Chairs: Dr. Oleg Siidra, Dr. Claire Colin

MS16-01

Novel structures of U minerals and compounds: from natural to synthetic crystals

Jakub Plášil¹

 Institute of Physics, Academy of Sciences of the Czech Republic, Praha, Czech Republic

email: plasil@fzu.cz

In Nature, uranyl minerals occur as important alteration products formed during weathering of uraninite, UO2+x, also referred to as oxidation-hydration weathering; it is of interest because of its analogy to the alteration of UO_{2+x} in the spent nuclear fuel [1]. Crystal structures of uranyl minerals are known for their remarkable compositional diversity and topological variability. In past few years, our knowledge of the uranyl crystal-chemistry has increased a lot; nevertheless, since the most recent overview summarizing 610 inorganic and 117 mineral structures [2] substantial discoveries have been made. Among them, it should be mentioned a discovery of the first natural uranyl mineral that contains nano-scale clusters in the mineral ewingite, Mg₈Ca₈(UO₂) 24(CO3)30O4(OH)12(H2O)138, which is nowadays considered as the most complex mineral structure in Nature [3]. Some novel structure topologies are growing every year along with finds of new minerals and efforts to synthesize novel materials in laboratories.

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Keywords: uranyl, crystal structure, topology

MS16-O2

New functional ferroics through crystallography

John Claridge¹

1. Department of Chemistry, Liverpool, United Kingdom

email: j.b.claridge@liv.ac.uk

A large fraction of functional materials used today are based on ferroic materials, in which the modulation or switching of the ferroic order parameter by temperature, pressure, electric or magnetic field, produces the functional property (e.g., permittivity, piezoelectricity, magnetoresistance) as used in devices. As most functional coefficients are highly sensitive to lattice softening at ferroic phase transitions, one of the main tools to engineer these materials for optimal performance is formation of solid solutions, where phase transition temperatures can be tuned to lie within or without the device's operating range. This strategy is widespread in oxide perovskites e.g., PbZrO3-Pb-TiO₃ (PZT), where the Zr/Ti ratio is adjusted to coincide with a morphotropic phase boundary (MPB) between the rhombohedral (R, polarisation P along [111],) and tetragonal (T, P along [100],) symmetries, at which the piezoelectric charge coefficient and other performance characteristics maximize. However, the science controlling the properties of solid solutions is complex and insufficiently understood to enable accurate prediction of the success of such strategies, thus frustrating materials design. By consideration of the chemical control of this relationship between local and average structure, significant progress has been made in materials design. We utilised a design approach exploiting the nanoscale information available from Reverse Monte Carlo analysis of pair distribution function (pdf) data from total scattering experiments that treats Bragg and non-long-range-order derived scattering equally. The Liverpool and Leeds team used this total structure approach to identify a new lead-free MPB family. Neutron pdf analysis of the lead-free polar R phase BiTi3/8Fe2/8Mg3/8O3 (BTFM)1 revealed two key features that were exploited to isolate a T symmetry Bi-rich perovskite. This T phase was then used to construct an MPB with R BTFM. Further, this new T phase forms a complete solid solution with R BTFM that affords a complex structure not purely due to either end-member with a maximum in d₃₃ i.e., an R-T MPB with a Curie temperature of over 600 °C.2 This MPB is sufficiently robust to permit an increase of Fe content to 68% that generates room temperature weak ferromagnetism while retaining switchable polarisation:3 a room temperature magnetoelectric ferromagnetic ferroelectric by incorporation of magnetic percolation into the original pdf-inspired MPB.

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Keywords: piezoelectric, ferroelectric, magnetoelectric

MS16-O3

Metal-organic frameworks with controllable arrangements of multiple metal cations

Celia Castillo¹, Víctor Antonio de la Peña-O'Shea², Inés Puente-Orench³, Enrique Gutierrez-Puebla¹, Felipe Gándara¹, M. Ángeles Monge¹

- 1. Institut of Materials Science of Madrid (CSIC), Madrid, Spain
- 2. IMDEA Energy, Madrid, Spain
- 3. Institut Laue Langevin, Grenoble, France

email: castillo@icmm.csic.es

The combination of multiple metal elements within a same structure is highly desirable because the resulting materials might exhibit new or enhanced properties. Metal-organic frameworks (MOFs) offer a suitable platform to incorporate multiple metal elements; however multi-metal MOFs typically appear as solid solutions with lack of control over the distribution of the selected elements. We have developed a multi-metal MOF system based on a helical-shaped secondary building unit (SBU), which is able to incorporate zinc, manganese, cobalt, calcium and/or magnesium in a controllable manner. The combination of these elements at selected molar ratios results in the addressed realization of multi-metal arrangements with precise, atomic control over their location in the SBUs. Structural elucidation of the resulting elemental sequences is possible through the combination of different techniques including single crystal X-ray diffraction, neutron powder diffraction, electron microscopy and energy-dispersive X-ray spectroscopy.



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Keywords: MOFs, multication, characterization

MS16-O4

Disorder–order transitions in the perovskite metal–organic frameworks [(CH₃)₂NH₂] [M(HCOO)₃] at high pressure

Ines Collings¹, Maxim Bykov², Elena Bykova³, Michael Hanfland¹, Sander van Smaalen⁴, Leonid Dubrovinsky², Natalia Dubrovinskaia⁴

- 1. European Synchrotron Radiation Facility, Grenoble, France
- 2. Bayerisches Geoinstitut, University of Bayreuth, Bayreuth, Germany
- 3. Deutsches Elektronen-Synchrotron, Hamburg, Germany
- 4. Laboratory of Crystallography, University of Bayreuth, Bayreuth, Germany

email: ines.collings@esrf.fr

The dimethylammonium metal formate compounds with the perovskite architecture have attracted interest over the years due to the coexistence of electric and magnetic orders [1], which in the case of the iron analogue, can be coupled [2]. The interesting physical properties are observed upon cooling, with a disorder-order transition at 160-270 K that originates from the loss of dynamic disorder of the dimethylammonium cation (DMA) [1,3], and an antiferromagnetic ordering for the magnetically active M2+ cations below 35-8 K [1]. The hydrogen bonding interaction from the DMA cation to the formate can allow for magnetoelectric coupling within certain compositions [2]. However, the temperatures needed for the multiferroic behaviour in these materials are below 35 K, and the coupling between the magnetic and electric orders are very weak. In an effort to explore different structural configurations with potentially improved physical properties, we study the dimethylammonium metal formates under pressure. In particular, we explore the possibility of inducing a disorder-order transition of DMA through reducing the volume using pressure. Similar structural configurations may then be replicated at ambient conditions by using "chemical pressure" through selection of different sized chemical components during synthesis.

High-pressure single-crystal X-ray diffraction is presented for the dimethylammonium metal formates (DMAMF), $[(CH_3)_2NH_2][M(HCOO)_3]$ where M = Mn²⁺, Fe²⁺, and Cu²⁺, in order to compare the high-pressure phases with the known low-temperature ferroelectric (for DMAMnF) and multiferroic (for DMAFeF) phases. The ambient phases of dimethylammonium metal formates were stable up to 5.53(3), 5.7(3), and 7.3(2) GPa for DMAMnF, DMACuF, and DMAFeF, respectively. After these pressures, phase transitions occurred that were initiated by the structural distortion of the metal formate framework. The impact of the high-pressure distortions on the dynamic disorder of the dimethylammonium cation for DMAFeF and DMAMnF, and the Jahn-Teller distortion for DMACuF will be discussed. In the case of DMAFeF, the experiment was in addition conducted with a penetrating pressure-transmitting medium (PTM) that resulted in a different pressure-dependent behaviour due to the PTM inclusion.

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Keywords: perovskite metal–organic frameworks, high pressure, disorder–order transitions

MS16-05

Lattice gas models and thermodynamics of gas uptake by porous materials from diffraction experiments

Dmitry Chernyshov¹, Iurii Dogaliuk¹, Yaroslav Filinchuk²

- 1. Swiss-Norwegian BeamLines at the European Synchrotron Radiation Facility, Grenoble, France
- 2. Université Catholique de Louvain, Louvain-la-Neuve, Belgium

email: dmitry.chernyshov@esrf.fr

Adsorption by a flexible small pore structure is frequently accompanied by a cooperative behavior; structural breathing [1] and hysteresis without phase transitions [2] may serve as examples of such a response. Collective phenomena associated with guest uptake by porous structures are of a practical interest for control of adsorption and selectivity as well as for fundamental research of cooperative effects in complex systems. We recently applied an Ising-like lattice gas model to rationalize a cooperative adsorption in porous materials. [3] A multi-site extension of the model with cooperative inter-pore and intra-pore guest-guest interactions specific for MOFs and alike materials is discussed here. Theoretical scenarios are compared with experimental observations provided by in-situ powder diffraction of synchrotron radiation analysis of active crystallographic sites and their occupancies. Elastic deformations of the host structure conjugated with pore population/depopulation is proposed as a basis of indirect cooperative interactions between guest molecules.

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Keywords: porous materials, gas adsorption, thermodynamics

MS17 Biominerals and bioinspired materials

Chairs: Prof. Wolfgang Schmahl, Dr. Anna Schenk

MS17-01

Cracking the structural and morphogenetic basis of tooth biomineralization in snailcrushing cichlid fishes

Elena Sturm¹, Jennifer Knaus¹, Claudius Kratochwil², Davide Carnelli³, Jana Segmehl⁴, Song Chen¹, Baohu Wu², Marina Krumova¹, Sebastian Sturm⁵

- 1. Department of Chemistry, University of Konstanz, Konstanz, Germany
- 2. Jülich Centre for Neutron Science at Heinz Maier-Leibnitz Zentrum Forschungszentrum Jülich, Garching, Germany
- 3. Department of Materials, ETH Zürich, Zürich, Switzerland
- 4. Institute for Building Materials, ETH Zürich, Zürich, Switzerland
- Institute for Solid State Research, Leibniz Institute for Solid State and Materials Research Dresden, Dresden, Germany

email: elena.sturm@uni-konstanz.de

The teeth of cichlid fishes provide a powerful model for how vertebrates optimize dental hard tissues for ecologically relevant tasks. [1] Cichlid fishes have undergone explosive speciation in a very short time span, evolving tuning morphological specializations. Dramatic variability in the shapes and inner structures of their teeth and jaws are central to their diversification. [2] The main task of this research work is to determine the structure-property relationships of dental hard tissues of Cichlid fishes (so called "soft" and "hard" diet species) through detailed investigation of the composition, hierarchical structure and their mechanical performance. The most exiting are those Cichlid species that have repeatedly evolved exceptionally robust teeth to crush snails. Thus, we elaborate and combine an exciting evolutionary model system with cutting-edge spectroscopy, microscopy and diffraction techniques to analyze structural, chemical and morphogenetic basis of biomineralization process of dental hard tissues. Our new understanding of tooth structure and morphogenesis in cichlids could also advance strategies for synthesizing biomimetic materials for biomedical application. [3-4]

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Keywords: biomineralization, dental hard tissues, cichlid fish

MS17-O2

Crystallization of biomimetic calcite aggregates in hydrogel systems

Lurdes Fernández-Díaz¹, Erika Griesshaber², Xiaofei Yin², Fitriana Nindiyasari³, Martina Greiner², Florian Weitzel², Andreas Ziegler⁴, Wolfgang Schmah²

- 1. Department of Mineralogy and Petrology, Complutense University of Madrid (UCM) & IGEO (ICMM, CSIC), Madrid, Spain
- Department f
 ür Geo- und Umweltwissenschaften, Ludwig-Maximilians-Universit
 ät, Munich, Germany
- 3. NRG, Le Petten, Netherlands (Holland, Europe
- Central Facility for Electron Microscopy, University of Ulm, Ulm, Germany

email: lfdiaz@geo.ucm.es

The formation of biological hard tissues takes place in hydrous gelatinous environments rich in polysaccharides, proteins and glycoproteins. These organic components are arranged in compliant three-dimensional matrices that direct the crystallization of the mineral component, within which they become occluded as porous membranes and networks of fibrils. The composite nature of biological hard tissues together to their distinct hierarchical architecture provide them with enhanced mechanical properties that are highly desirable in man-made materials. Designing successful routes to produce high-performance bio-inspired organic-inorganic composites relies on our understanding of the parameters that control the occlusion of organic matrices within growing crystals and the effect that this occlusion has on the micro-structuring of the mineral. Artificial hydrogels that have traditionally been used as crystallization platforms to produce large crystals of sparingly soluble phases share numerous features with the organic matrices found in hard tissues. Interestingly, these hydrogels also become occluded within crystals during growth. The way of gel occlusion is distinct and relates to characteristics that are specific of the type of hydrogel, like the nature of the interactions that hold its matrix together and its porosity.1 Gel occlusion is further modulated by physicochemical conditions in the system, which determine supersaturation and growth rate, and their evolution.2 Here an overview of the morphological and microstructural characteristics, as uncovered by Field Emission Gun Scanning Electron Microscopy (FEGSEM) and Electron Backscattered Diffraction (EBSD), of gel-calcite composites grown in a variety of gels (silica, gelatin, agar, agarose, and gelatin-agarose mixtures) is presented. Differences in amount and organization of occluded gel polymeric matrices within the composites are discussed taking into consideration the gel mechanical response to crystallization pressure. Finally, a correlation between the characteristics of occluded gel distribution and microstructural features of the composites is stablished.

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MS17-O3

Induced nucleation of biomimetic calcium phosphates on 3D-printed porous polymer micro-scaffolds

Jaime Gómez-Morales¹, Luis Antonio González-Ramírez¹, Youen Vitry², Pierre Lambert², Isaac Rodríguez-Ruiz³

- Laboratorio de Estudios Cristalográficos, Instituto Andaluz de Ciencias de la Tierra. CSIC-Universidad de Granada, Armilla, Spain
- Transferts Interfaces et Procédés, Université Libre de Bruxelles, Brussels, Belgium
- Research Department on Mining and Fuel Reprocessing Processes. CEA, DEN, Bagnols-sur-Cèze, France

email: jaime@lec.csic.es

Heterogeneous nucleation and growth of calcium phosphates (hereafter CaP) on polymer substrates is of great relevance for the preparation of bioactive scaffolds for non-load bearing applications in bone tissue engineering.¹ In the last years we have developed a new synthetic route to precipitate biomimetic apatite (Ap) nanoparticles, which has been employed to deposit CaP films on mica muscovite sheets.² The precipitation process, based on the vapour diffusion sitting drop micro-method, is performed in a closed two–chamber environmental micro-reactor called *crystallization mushroom*.² The deposition of CaP is here driven by diffusion of both CO₂ and NH₃ (generated *in situ* by decomposition of NH₄HCO₃) through microdroplets containing Ca²⁺ and HPO₄²⁻ ions, where substrates are dipped.

In this research³, preliminary precipitation experiments have been carried out using as model supports flat lamellae of different commercial polymer-such as OSTEMER, SU-8 and PDMS and the polymer-ceramic composites ORMOCORETM and ORMOCLADTM, all of them allowing 2D and 3D microfabrication techniques. Optimal reagent concentrations of the 40 µL aqueous droplets inside the mushroom were 50mM Ca(CH₃COO)₂ + 30mM (NH₄)₂HPO₄ (Ca/P=5/3) whereas 3 mL of a 40mM NH₄HCO₃ solution were put in the chamber acting as reservoir. Under these conditions, and after 7 days of vapour diffusion, the deposited CaP films presented a composition of apatite plus octacalcium phosphate (OCP) in some of them, and different thicknesses, as confirmed by SEM, XRD and Raman spectroscopy.

In a second step, several prototypes of 3D printed scaffolds of cubic shape and ~1 mm long, have been CAD-designed and prepared by the direct laser writing (DLW) technique using an IP-L 780 photoresist. These scaffolds are endowed of uniaxial and interconnected porosity with a controlled pore size within the range 25 µm-100 µm. The CaP nucleation experiments, using these specimens as supports, were carried out using the same biomimetic route under similar reagent concentrations as determined before, and time of about 30 days. Prior to mineralization the scaffolds were dipped in a 0.1 M HNO₃, then they were rinsed with deionized water and the intraporous air removed by means of a vacuum pump. The results show the full mineralization of the scaffolds, both externally and internally inside the pores, coating the full available surface area. It is concluded that combining the 3D DLW technique with this biomimetic route is a promising methodology to prepare hybrid bioactive mineralized porous scaffolds for some valuable ad-hoc applications in bone tissue engineering.

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Keywords: calcium phosphates, polymer scaffolds, 3D-microprinting

MS17-O4

The directing effects of bacterial EPS and artificial hydrogel matrices on calcite crystal organization in EPS-hydrogelcalcite composite aggregates

Xiaofei Yin¹, Florian Weitzel¹, Erika Griesshaber¹, Concepción Jiménez-López², Lurdes Fernández-Díaz³, Andreas Ziegler⁴, Alejandro Rodríguez-Navarro⁵, Wolfgang. W. Schmahl¹

- 1. Department of Geo- and Environmental Sciences, Ludwig-Maximilians-Universität München, Munich, Germany
- 2. Department of Microbiology, Universidad de Granada, Granada, Spain
- Department of Crystallography and Mineralogy, Universidad Complutense de Madrid, Madrid, Spain
- 4. Central Facility for Electron Microscopy, Universität Ulm, Ulm, Germany
- 5. Department of Mineralogy and Petrology, Universidad de Granada, Granada, Spain

email: xiaofei.yin@campus.lmu.de

Mineralized structures generated under biological control are hierarchical composites that consist of two distinct materials: a compliant biopolymer matrix that is reinforced by stiff and hard minerals. In gastropod, bivalve, brachiopod shells the biopolymer matrix consists of two components: (i.) matrix membranes that subdivide space and influence shape and size of mineral units, (ii.) foam-like networks of fibrils occluded within the mineral units that control attachment and orientation of crystallites. Microbial cells surround themselves with a gelatinous coating: EPS (extracellular polymeric substances) that consists of polysaccharides, proteins, lipids and occurs in a wide range of molecular sizes, conformations, and physical/chemical properties. The EPS fabric is a three-dimensional fibrous scaffold that protects bacterial cells and allows them to orient themselves. Numerous bacteria precipitate carbonate as a by-product of their metabolic activity. The latter induces supersaturation with respect to carbonate phases in microenvironments within the EPS fabric[1].

Recent studies^[2] have shown that in biocarbonate hard tissues organic membranes and fibres control mineral organization within the basic mineral units. The assembly pattern of the biomineral is adjusted according to the fabric of the preformed organics. In order to understand the influence of biopolymer membranes and fibres on mineral organization, we conducted EPS/agar gel/calcite growth experiments and investigated membrane formation, mineral/EPS/agar gel interlinkage and mineral organization in the composite aggregates. We used EPSs secreted by four different bacteria: the gram-positive bacterium Bacillus subtilis and the gram-negative bacteria Pseudomonas putida, Mycobacterium phlei and Mycobacterium smegmatis. Characterization was performed with HR-SEM imaging; patterns of mineral orientation were measured with electron backscatter diffraction (EBSD).

The EPS scaffold exerts a significant influence on aggregate morphology, the presence of membranes and their distribution within the aggregate and calcite crystal organization in the composites (Fig. 1). Membrane formation is extensive and is highly increased relative to composite aggregates grown without EPS. Rhombohedral morphologies are absent; aggregate and calcite crystal morphologies and surfaces are always rounded. The aggregates are radial mosaic crystals, with their individual subunits not being substructured (Fig. 1). Calcite crystal co-orientation strength and patterns range from markedly co-oriented (Fig. 1d) over graded (Figs. 1c, 1a), to very little co-oriented (Fig. 1b). Hence, EPS incorporation within the calcite modulates the mineral microstructure and texture in a manner that is characteristic for the EPS of a specific bacterium. These characteristics could be used as a tool for identifying biologically induced calcification in the geological record^[3].



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Keywords: bacteria EPS, mineral organization, EBSD, biomarker

MS17-05

Crystallographic characterisation of fluorapatite based glass-ceramics synthesised from industrial waste

Siegbert Schmid1, Chee Wah Loy1

1. School of Chemistry, The University of Sydney, Sydney, Australia

email: siegbert.schmid@sydney.edu.au

Apatite based glass-ceramics have been extensively studied in recent decades. They show excellent mechanical properties, bioactivity and compatibility for biomedical applications. They can form an apatite layer and strong chemical bonds at the bone or tooth interface with the implant [1]. The nano-crystalline structures, bioactivity and mechanical strengths of such glass-ceramics depend on their parent glass composition and the crystallisation processes during sintering.

A series of phase transformations of novel calcium fluoraluminosilicate (CFAS; SiQ-Al₂O₃-A₂O₃-CaO-CaF₂) glasses forming a range of fluorapatite based glass-ceramics on sintering are reported. The sintering process induces formation of fluorapatite, mullite and anorthite phases within the amorphous silicate matrices of the glass-ceramics. The glasses are partially prepared from waste materials such as rice husk ash, pacific oyster shells and disposable aluminium cans. The thermally induced crystallographic and microstructure evolution of these glasses towards fluorapatite glass-ceramics, with applications in dental and bone restoration, are investigated by a range of techniques, including powder X-ray diffraction as well as small angle X-ray and neutron scattering techniques [2].

The observed phase transformations of glasses to glass-ceramics for the investigated compositions enhance our understanding of the effects of glass composition and sintering temperatures on the phase transitions in glass-ceramics. All investigated glasses produce fluorapatite glass-ceramics on sintering at temperature around 800 °C. The optimum glass compositions and sintering temperatures to produce fluorapatite-mullite, fluorapatite-anorthite and fluorapatite-albite glass-ceramics have been identified from PXRD analysis and will be presented. Formation of fluorapatite in glass-ceramics can also be identified from the far-infrared spectrum in agreement with the PXRD results. The fluorapatite glass-ceramics contain crystalline fluorapatite domains dispersed in an aluminosilicate glass matrix. This can be verified from FESEM imaging and the analysis of SANS data. The SANS results provide information about the average size of the fluorapatite domains in glass-ceramics. SANS data were interpreted using the correlation length model. The correlation length parameter obtained from the fit can be correlated with the average sizes of crystalline domains in these glass-ceramics.

The suitability of the investigated CFAS glasses to produce glass ionomer cements for dental restoration has been assessed and found to be comparable to the standard LG26 glass, thereby demonstrating the feasibility of using waste materials to develop biomaterials for bone and dental restoration.

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Keywords: glass-ceramics, small-angle scattering, fluorapatite

MS18 Crystallography at high pressure and dynamically compressed matter

Chairs: Dr. Damian Paliwoda, Dr. Ines Collings

MS18-01

X-Ray diffraction studies of mineral phase transitions under shock compression

Sally June Tracy1

1. Geosciences, Princeton University, Princeton, United States of America

email: sjtracy@princeton.edu

Laboratory shock wave experiments have long played an important role in the study of geological materials under extreme pressure and temperature conditions. Shock compression experiments provide the unique capability to study impact phenomena in real time and allow for measurements of equations of state and phase transitions. However, a limitation of continuum shock wave studies is that the crystal structure of high-pressure phases formed under dynamic compression is generally not known. This talk will focus on new experiments carried out at the Dynamic Compression Sector (DCS) of the Advanced Photon Source. DCS couples gun-based dynamic compression platforms with time-resolved synchrotron X-ray diffraction. This allows for an in situ study the crystal structure of minerals shocked into the high pressure and high temperature conditions that occur in the Earth's interior or during meteorite impacts. The diffraction data are combined with continuum-level measurements to reveal a complete picture of the material response from the atomic length scale to the continuum level, allowing for the unambiguous determination of the phase(s) formed under shock compression at ~100 ns timescales. This talk will review recent experiments carried out at DCS on materials including SiO₂, TiO₂ and ZnO. The resulting diffraction patterns are used to identify the high-pressure mineral structures and texture analysis of data for shocked single crystals can provide insight into transformation pathways between low- and high-pressure phases. The findings improve our understanding of minerals in the Earth's deep interior and allow us to better understand crystal structure modifications that occur in shocked minerals during meteorite impact events.

Keywords: shock, Hugoniot

MS18-O2

High-pressure studies on magnetocaloric materials

Karen Friese¹, Andreas Eich², Paul Hering¹, Martin Meven³, Andrzej Grzechnik²

- Jülich Centre for Neutron Science-2, Forschungszentrum Jülich GmbH, Jülich, Germany
- Institute for Crystallography, RWTH Aachen University, Aachen, Germany
- Institute of Crystallography, RWTH Aachen University and Jülich Centre for Neutron Science, Forschungszentrum Jülich GmbH at Heinz Maier-Leibnitz Zentrum (MLZ), Garching, Germany

email: k.friese@fz-juelich.de

The magnetocaloric effect describes the change of the adiabatic temperature of a material with the application of a magnetic field. This effect forms the basis of magnetic refrigeration technologies that could potentially replace conventional vapor compression cooling. Individual compounds in the system Mn5, Fe, Si3 (all of them hexagonal at ambient conditions) undergo a variety of magnetic phase transitions as a function of temperature and composition which are accompanied by a significant (for some compounds inverse) magnetocaloric effect [1,2]. The magnetic transitions are also clearly reflected in changes of the crystal lattice [2]. The application of hydrostatic pressure changes the interatomic distances in the crystal structure and strongly influences the magnetic exchange interactions. Pressure experiments can therefore provide crucial information on magnetocaloric materials and help to understand the fundamental mechanism of the magnetocaloric effect. We performed in situ temperature dependent powder diffraction experiments at high pressures at synchrotron sources (Petra III and ESRF), as well as in situ high pressure single crystal diffraction experiments at laboratory sources and complementary magnetization measurements under high pressure. In addition, we are currently developing the experimental setup for high pressure neutron diffraction experiments using thermal neutrons at the single crystal diffractometer on the hot source (HEiDi) at the MLZ in Garching where first results show that the diffraction data collected at HEIDI can be used for full and reliable structure refinements [3]. Our experiments on the magnetocaloric compounds show that the magnetic properties are strongly influenced by the application of hydrostatic pressure. The effect of pressure on the unit cell volume is similar to the effect of chemical substitution (or "chemical pressure"), as the substitution of Mn by the smaller Fe in the series Mn_{5-x}Fe_xSi₃ also leads to a reduction of the unit cell volume. A detailed comparison of hydrostatic and "chemical pressure" will be provided. On the other hand, a detailed comparison of the influence of pressure and temperature on the studied materials surprisingly shows that the degree of distortion of the (hexagonal) unit cell is far more sensitive to temperature than to pressure - a fact that is probably closely related to the magnetocaloric properties of the materials.

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Keywords: High pressure, single crystal diffraction, magnetocaloric materials

MS18-O3

Crystallographic phase transition in singlecrystal and powder form, probed by in situ X-ray diffraction under pressure

Elodie Tailleur¹, Mathieu Marchivie¹, Patrick Rosa¹, Jean-Paul Itié², Philippe Guionneau¹

1. ICMCB-University of Bordeaux, Bordeaux, France 2. Synchrotron SOLEIL, Gif-sur-Yvette, France

email: tailleur.elo@gmail.com

Getting high pressure structural data still appears a challenging investigation, notably in the field of molecular materials. Despite a significant improvement of X-ray diffraction methods and an increasing number of crystal structures under high pressure, structure-properties relationship under pressure are rather rare and the microstructural scale is almost unexplored. We have studied a compound having a structural phase transition upon applying pressure whose phases are characterized by different magnetic properties [1]. The present work aims to determine the structural properties under pressure at different scales, from the coordination sphere of the metal center to the crystal packing scale by in situ Single-Crystal X-Ray Diffraction (SCXRD) and to correlate them to magnetic properties. Moreover, in situ high-pressure Powder X-Ray Diffraction (PXRD) synchrotron experiments have been performed and provide not only an investigation of microstructural properties under pressure but also a fine track of the transition as a function of pressure. In situ PXRD under pressure revealed the behavior of the phase transition including **piezo-hysteresis** [2]. Finally, piezo-hysteresis has been explored by combining high pressure and variable temperature PXRD leading to unexpected behaviors. This work deals with a promising molecular compound with a pressure-induced spin-crossover at relatively low pressure, about 1.6 kbar, opening potential piezo-switch based applications.



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Keywords: Pressure, in situ XRD, Piezo-hysteresis

MS18-O4

Penta- and octahedrally coordinated P and Be in high-pressure phases of CaB₂Si₂O8

Anna Pakhomova¹, Georgios Aprilis², Maxim Bykov², Liudmila Gorelova³, Sergey Krivovichev³, Leonid Dubrovinsky²

- 1. Deutsches Elektronen Synchrotron, Hamburg, Germany
- 2. Bayerisches Geoinstitut, University of Bayreuth, Bayreuth, Germany
- 3. Saint-Petersburg State University, Saint-Petersburg, Germany

email: anna.pakhomova@desy.de

Recent advances in diamond anvil cell techniques combined with third-generation synchrotron facilities enabled *in situ* monitoring of crystal structure evolution up to ultrahigh pressures by means of single crystal X-ray diffraction (SCXRD). Recent synchrotron-based experiments have revealed a number of high-pressure polymorphs that are very unusual for the conventional crystal chemistry. One of such examples is danburite, CaB₂Si₂O₈, that follows a step-wise transitions resulting in changes of Si coordination from tetrahedral to octahedral through an exotic trigonal bipyramidal geometry [1]. The discovery of this transformation route has motivated us to investigate the high-pressure behaviour of isotopological mineral hurlbutite, CaBe₂P₂O₈.

SCXRD experiments were performed at the P02.2 beamline at synchrotron Petra III up to 91 GPa. At ambient conditions the crystal structure of hurlbutite (sp.gr. $P2_1/c$) is built on PO₄ and BeO₄ tetrahedra polymerizing through common vertices with formation of framework featuring four- and eight-membered channels. The 8-membered rings are occupied by Ca atoms. Up to 7.5 GPa conventional continuous contraction of unit-cell parameters is observed. The compression up to 7.5 GPa is controlled by changes in T-O-T angles while the TO₄ tetrahedra stay rigid. Above 7.5 GPa the b and c axes continue to decrease, while the a axis reveals an anomalous increase. This behavior indicates a change in a compression mechanism: half of TO4 units undergo progressive pressure-induced geometrical distortion. Above 70 GPa the crystal structure undergoes displasive phase transition that is induced by increase of P and one Be coordination number. The new polyhedra of penta-coordinated phosphorus and beryllium possess trigonal bipyramid geometry with two long apical bonds (1.662-1.813 Å for P and 1.711-1.798 Å for Be) and three short equatorial bonds (1.471-1.506 Å for P and 1.492-1.545 Å for Be). Upon further compression above 90GPa, the appearance of a new phase, co-existing with hurlbutite-II, is observed. The structure of new phase, hurlbutite-III, was solved and refined in the P-1 space group. All B and P are octahedrally coordinated with P-O bonds of 1.49-1.77Å and Be-O bonds of 1.50-2.08 Å.

While there are rare reports on existence of P[V] and P[VI] [2,3], the Be[V] and Be[VI] have been not reported before. Hurlbutite-III is the first example of the phase containing the element of the second group in six-fold coordination. The nature of the hypervalent Be-O bonding and the differences between high-pressure routes of danburite and hurlbutite will be discussed.

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Keywords: high-pressure structural analysis; phase transitions; coordination number

MS18-O5

Thermal diffuse scattering. A novel approach for probing elasticity at extreme conditions

Bjoern Wehinger¹, Alessandro Mirone²

- 1. Department of Quantum Matter Physics, University of Geneva, Geneva, Switzerland
- 2. European Synchrotron Radiation Facility, Grenoble, France

email: bjorn.wehinger@unige.ch

I will present a novel and fully quantitative analysis of thermal diffuse x-ray scattering. High-precision measurements of diffuse scattering intensities together with a rigorous data analysis now allow for the determination of the full elasticity tensor in a single crystal diffraction experiment [1], see Figure 1.

Our approach enables a reliable and model-free determination of the elastic properties and can be performed together with crystal structure investigation in the same experiment. Elastic moduli can be extracted from small single crystals of arbitrary symmetry, shape and optical properties and will allow for significant progress in the study of the elastic behaviour of minerals at geophysical relevant conditions, structural phase transitions and fundamental interactions of phonons with other quasi-particles. I will furthermore show that this approach can be applied to high pressure, were the simultaneous measurement of structure and elasticity provides the possibility to establish a primary pressure scale from a single measurement.

Figure 1. Measured (left panel) and calculated (right panel) thermal diffuse scattering from calcite at T = 170 K. The images show a cross-section of the reciprocal space in Cartesian coordinates, in the vicinity of the [1, 0, 16] reflection. Scattering intensities are shown on a linear color scale from black (zero) to white (maximum intensity).



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Keywords: diffuse scattering, elasticity

MS19 Materials on energy saving and climate sustainability

Chairs: Dr. Klaudia Hradil, Dr. Claudia Weidenthaler

MS19-01

Carbon dioxide fixation in succulent plants: a crystal engineering, solid state modeling and kinetics approach

Ebrahiem Botha1, Andreas Roodt1

1. Chemistry, University of the Free State, Bloemfontein, South Africa

email: ebotha@ufs.ac.za

Photosynthesis in plants is the production of sugar-like entities utilizing carbon dioxide fixation. The equivalent amount of oxygen is produced as 'by-product'. For this conversion to be effective, the plant uses different mechanisms for CO₂ fixation. These mechanisms rely on direct access to the Calvin cycle during daytime, where different forms of pyruvate/pyruvic acid are utilized to produce the sugars. Alternatively, indirect access to the Calvin cycle via the preceding Crassulacean Acid Metabolism (CAM) process, may proceed under special conditions of plant stress, or in general in typical Succulent plant families. Storage of the carbon dioxide in different forms of malate/malic acid involves the absorption of the CO2 (often/ principally at night when the stomata open), and then availing it during the next light absorption sequence (closed stomata to preserve moisture) to enter the Calvin cycle. In this project, we aim to fundamentally investigate the physical and chemical processes of carbon dioxide fixation. This we do by using artificial model 'plant leaf analogs', by crystal engineering of appropriate active systems. Therefore, further enabling the utilization of the carbon dioxide as value-added building block for synthetic methodologies via biomimetic strategies.

A series of rhodium and other platinum group metal complexes, including carboxylates were synthesized to mimic the active systems in the plant leaves that were probed using a plant sample box we custom-built for the project. Some rhodium model systems, wherein different non-labile bidentate ligand systems with different stereo-electronic properties have been included, were evaluated kinetically. The complexes were characterized using NMR, FTIR, UV/ vis and SC-XRD. These complexes include simple square planar geometries with labile ligand systems to mimic (reactive) carbon dioxide models. Preliminary kinetics were studied to evaluate both steric and electronic effect at these metal centers.

Selected complexes were also studied by single crystal X-ray crystallography to verify the bonding modes of the bidentate ligands therein, as well as the carbon dioxide and model ligands' coordination geometries.

Selected details of these compounds will be discussed in this presentation as well as some future strategies to be followed.

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Keywords: Succulents, Crystallography, Kinetics
MS19-O2

Operando neutron diffraction study of crystal structure changes in LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ cathode material

Ivan Bobrikov¹, Natalya Samoylova¹, Sergey Sumnikov¹, Olga Ivanshina¹, Roman Vasin¹, Anatoly Balagurov¹, Roman Eremin², Katerina Kornieieva³, Pavel Zolotarev²

- 1. Condensed Matter Department, Joint Institute for Nuclear Research, Dubna , Russia
- 2. Samara Center for Theoretical Materials Science, Samara, Russia
- 3. Joint Institute for Nuclear Research, Dubna , Russia

email: bobrikov@nf.jinr.ru

LiNi_{1,xy}Co_xAl_yO₂ ($x \approx 0.15$, $y \approx 0.05$) oxide (NCA) is one of the most common cathode materials used for the Li-ion batteries production. Its advantages include high practical capacity (~200 mA · h/g) and discharge voltage (~3.8 V), rather low cost, structural stability during electrochemical cycling and a relatively low capacity loss per cycle. NCA material was intensively studied during the last decade, but abnormal behavior of NCA crystal structure (phase separation, nonlinear changes of interlayer distances) during the first and consequent cycles had not been clearly explained until recently. We have applied operando neutron diffraction, combined topological analysis as well density functional theory modeling to study NCA crystal structure changes [1-3]. Due to high penetration possibility of neutrons a part of experiments has been made on a commercial 18650 battery with NCA cathode [1]. For crystal structure study of NCA during the first cycle a new electrochemical cell has been developed [3]. Measured dependencies of interatomic spacing and interlayer spacing of the cathode structure on the lithium content are explained by several factors, such as variations of oxidation state of cation in oxygen octahedra, Coulomb repulsion of oxygen layers, changes of average effective charge of oxygen layers and van der Waals interactions between MeO2-layers at high level of NCA delithiation. The phase-separated state at the first cycle is caused by the morphology of NCA material. These observations could be expanded to layered cathode materials with similar microstructures.

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Keywords: Lithium-ion battery, $LiNi_{0^{+8}}Co_{0^{+15}}Al_{0^{+05}}O_2,$ neutron diffraction

MS19-O3

Neutron diffraction studies of oxygen disorder in Nd_2NiO_{4+d}

Sumit Ranjan Maity¹, Lukas Keller¹, Juerg Schefer¹, Monica Ceretti², Werner Paulus²

- Laboratory for neutron scattering and imaging, Paul Scherrer Institute, Villigen, Switzerland
- Department o Institut Charles Gerhardt, CNRS-University Montpellier, Montpellier, France

email: sumit.maity@psi.ch

Better understanding of oxygen diffusion in non-stoichiometric oxides becomes essential for further development of intermediate temperature solid oxide fuel cells. In this prospect, rare earth nickelates (R2NiO4+d) emerged as promising materials in which oxygen transport is driven by oxygen disorder and non-stoichiometry. Their crystal structure consists of RNiO₃ perovskite layers sandwiched between RO-type rock salt layers and extra oxygens are intercalated in tetrahedral sites inside the rock salt layer. Oxygen diffusion, in these materials, is highly anisotropic and described by interstitialcy mechanism [1] in which excess oxygens diffuse via apical oxygens inside the rack salt layer. However, close to room temperature, diffusion is non-Aarhenius type but a lattice activated process [2]. In this talk, I will address structural studies which are performed with neutron diffraction on polycrystalline and single crystal Nd₂NiO₄₂₅ compound as a function of temperature, are essential to get experimental evidences on oxygen migration mechanism in these oxides. High resolution neutron diffraction studies show the evidence of 3d-ordering of excess oxygens in below 823 K, confirming the pinning of excess oxygens to the crystal lattice which makes the real structure incommensurate. The average structure (exclusing incommensurate superstructure reflections) of the compound can be described in orthorhmbic Fmmm space group. However, these incommensurate oxygen superstructure reflections start to lose intensity around 400 K and arround 823 K, loss of 3d-oxygen ordering occurs which is accompanied by a orthorhmbic to tetragonal structural transition. With scattering density studies of average structure using the Maximum Entropy Method, we observed unusually high anharmonic displacement factors both for equatorial and apical oxygen atoms showing large displacement amplitudes (fig. 1) towards [001] and [110] with respect to the F-symmetry cell, respectively which are getting amplified in the tetragonal phase. This result confirms the proposed interstitialcy diffusion mechanism for these oxides and supports previously reported molecular dynamics simulated results [3] on Nd2NiO425 compound. In conclusion, with neutron diffraction studies up to high momentum transfers, we show that excess oxygens are essential to activate large apical oxygen displacemnts toward nearest vacant interstital site allowing oxygen diffussion in the intermediate tempearture range.



Fig. 1. (a) Crystal structure of Nd/NO₂₂₂ in Freener space group (b)Anhamsonic displacements of apical oxygen atoms at room temperature for Nd/NiO₂₂₃ obtained with MEM. White lines represent F-cell.

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Keywords: Interstitialcy mechanism, Arrhenius-type diffusion, Anharmonic apical oxygen displacement.

MS19-O4

The aluminium-ion battery

Tilmann Leisegang¹, Tina Nestler¹, Falk Meutzner¹, Matthias Zschornak¹, Robert Schmid¹, Wolfram Münchgesang¹, Artem A. Kabanov², Vladislav A. Blatov², Dirk C. Meyer¹

- 1. TU Bergakademie Freiberg, Feiberg, Germany
- Samara State Technical University, Samara Center for Theoretical Materials Science, Samara, Russia

email: tilmann.leisegang@physik.tu-freiberg.de

The expansion of renewable energies and the growing number of electric vehicles and mobile devices demand for improved and low-price electrochemical energy storage. In order to meet the future needs for energy storages novel material systems with highest energy densities, readily available raw materials, and safety are required. Currently, especially lithium and lead dominate the battery market, but beside cobalt and phosphorous, in particular lithium may show substantial supply challenges in the future. Therefore, the search for new chemistries will become increasingly important in the future in order to diversify battery technologies.

Due to its high abundance and triple charge, aluminium is a highly interesting candidate for high-valent, *post*-lithium batteries, since for stationary application large quantities of active mass are necessary.

Within the crystalline structure of potential solid aluminium-ion conductors, the high charge of the trivalent aluminium ion poses the challenge of high attraction towards anions and high repulsion from cations. In this context, an optimised crystal structure is of paramount importance. By analysing the necessities for good ionic transport and applying this knowledge to large crystallographic databases by means of high-throughput crystal-chemical analyses, we address the identification of promising materials candidates for a future all-solid-state aluminium-ion battery technology.

Traditionally, the search for Al-conductors was started with oxygen-containing materials. We opened up the chemical space of potential aluminium-ion conductor materials by first analysing bonding differences in aluminium and oxygen, sulphur, or selenium-containing materials. Due to the decreasing electronegativity and increasing size, we found an increasing polarisation of the chalcogenides and a better shielding of charge from the aluminium-ions. We have studied varying ternary spinel-like structures by means of density functional theory (DFT) calculations to quantitatively evaluate the chemical bonding in aluminium-chalcogenides.

Eventually, this knowledge was applied to the ICSD to filter out promising materials for the conduction of aluminium-ions. We applied Voronoi-Dirichlet partitioning to first geometrically filter for materials with interconnected interstitial voids that are large enough to host aluminium-ions. Secondly, bond-valence site-energies were calculated to estimate respective activation energies for the percolation of aluminium-ion conduction paths. As a last step, DFT will is be used to simulate a full, dynamic diffusion process for the most interesting candidates *ab initio*.

We will present the current state of the aluminium-ion battery, including theoretical and first experimental results. This work is funded by the German BMBF (R2RBattery: 03SF0542A), the Russian Megagrant (14.B25.31.0005), and the RSF (16-13-10158).



Keywords: Battery, post-lithium, ion conductor

MS19-05

Investigating CO₂ uptake in Sc₂BDC₃ using XRD, *ab initio* DFT and GCMC methods

Jonathan Richardson¹, Jorge Sotelo¹, Stephen Moggach¹, Jamie McHardy¹, Carole Morrison¹, Tina Düren², Paul Wright³

- 1. School of Chemistry, University of Edinburgh, Edinburgh, United Kingdom
- 2. Centre for Advanced Separations Engineering, University of Bath, Bath, United Kingdom
- 3. School of Chemistry, University of St Andrews, St Andrews, United Kingdom

email: J.G.Richardson@ed.ac.uk

Despite the large number of MOFs that have been synthesised and are present in the Cambridge Structural Database, 84,185 as of Nov. 2017, very few have been studied for both their gas adsorption and mechanical properties.¹ Most investigations concerning the former are based upon adsorption isotherms and hence there is a lack of understanding concerning the location of adsorbed guest molecules within the pores and the nature of specific interactions between the guest molecules and the framework. Up to 2014, 120 crystallographic studies on frameworks containing adsorbed gas molecules had been reported, with only 47 frameworks investigated in all.² A more detailed understanding of these interactions will help us develop more insightful structure-property relationships, thereby aiding chemists in designing MOFs with enhanced or specific guest uptake.

The small-pore MOF Sc₂BDC₃ (where BDC = benzenedicarboxylate) was initially observed to undergo an orthorhombic-to-monoclinic phase transition, via rotation of one pair of BDC linkers, under CO₂ uptake at p = 1 bar and 235 K.³ Here, we have used a combination of capillary gas cell XRD experimental and *ab initio* DFT and GCMC computational methods to show that the framework also undergoes the same phase transition, gradually, at 298 K at higher CO₂ pressures (complete at 3 bar). Additionally, a third adsorption site, which was not seen in the original investigation at 235 K, was observed; this discovery verified the expected maximum uptake of CO₂.

Ab initio DFT calculations determined that the monoclinic form of Sc₂BDC₃ is the lower energy geometry-optimised structure (by 13.3 kJ mol-1); the orthorhombic phase however is present at 298 K due to the entropic term having greater weighting at this temperature. Therefore, the formation of the monoclinic phase at room temperature upon CO2 uptake is a result of CO2-framework interactions exceeding the energy barrier to linker rotation. This was shown using GCMC to model CO₂ uptake in the experimental framework structures, with stronger CO₂-framework interactions in the monoclinic phase. Additionally, there was good agreement between the binding site hierarchies observed by the three different methods, with a clear switching of the site hierarchy between the two phases. When a CO₂/CH₄ gas mixture was applied to this material, the XRD and computational methods showed that Sc₂BDC₃ has selectivity for CO₂ over CH4; this was a result of weaker CH4-framework interactions and specific CH4 adsorption site locations which allowed CO₂ to occupy its strongest adsorption site unhindered.

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Keywords: MOF, XRD, computation

MS20 Rating and improving data quality: instrumentation, analysis and postprocessing

Chairs: Dr. Karine Röwer, Dr. Loes Kroon-Batenburg

MS20-O1

Experimental charge density studies: improvements in data processing

Regine Herbst-Irmer1

 Institute of Inorganic Chemistry, University of Göttingen, Göttingen, Germany

email: rherbst@chemie.uni-goettingen.de

In experimental charge density investigation, it is indispensable to use the highest possible quality of data. Systematic errors should be avoided.

One systematic error is the low-energy contamination caused by focusing multilayer optics. To eliminate this problem filtering by interposition of a low-density material foil into the beam was proposed. However, filtering lowers the intensity, which might be crucial, especially for charge density data collection, and is of course not possible for already measured data. The low-energy contamination mainly affects the reflections with indices 3h 3k 3l. In the program SADABS [1], a 3λ correction in analogy to the earlier $2/\lambda$ correction is now implemented. [2]

In several charge density studies, we noticed that the residual density improved significantly after ten resolution dependent scale factors were refined. The dependency of the scale factors against resolution showed a typical pattern for all data sets, but the variation was much smaller for data collected at 15 K instead of 100 K. Therefore, this procedure seems to cure errors that are resolution and temperature dependent such as thermal diffuse scattering (TDS). Similar results could be obtained by processing data with relatively small integration boxes instead of refined box sizes. This procedure seems to emulate a rough TDS correction. However, to find the best integration box is very time consuming. In a nested interval approach, a correction factor { α = a[sin(9)/ λ]² + b[sin(9)/ λ]³} is determined that minimizes these errors and improves the model quality. [3]

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Keywords: data quality, low-energy contamination, thermal diffuse scattering

MS20-O2

Nonisomorphism - diagnostics and metrics

Kay Diederichs1

1. University of Konstanz, Department of Biology, Konstanz, Germany

email: kay.diederichs@uni-konstanz.de

Datasets measured from different crystals are affected by both random and systematic errors. Systematic errors may arise from different properties of the crystals (e.g. composition and conformation of molecules, or their hydration state) or from experimental conditions (e.g. beam fluctuations or detector non-linearities). Datasets differing systematically are called non-isomorphous, and current crystallographic procedures are far from being able to capture and analyse the various sources of systematic error.

Often, a correlation coefficient is used for inter-dataset comparison [1], but the relations between datasets are not obvious from the matrix of pairwise correlations since the numerical value of the correlation coefficient is lowered by both random and systematic differences. It is therefore desirable to develop methods that can separate random and systematic effects on data.

The talk presents a novel type of analysis [1] of the pairwise correlation coefficients which positions datasets within a low-dimensional space whose axes are associated with the types of systematic differences between the datasets. This dimensionality reduction can not only be used for classification purposes (e.g. to find out which datasets are so similar in their properties that they can be merged), but can also derive dataset relations on a continuous scale, and directly relates to previous work [3] which introduced CC1/2 for describing the precision of crystallographic data.

This novel analysis has numerous applications in Structural Biology, but also in other fields.



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Keywords: nonisomorphism, data quality, heterogeneity

MS20-O3

Combining a nine-crystal multianalyser stage with a Pilatus3 X CdTe detector for high-resolution X-ray powder diffraction at ESRF-ID22

Catherine Dejoie¹, Mauro Coduri¹, Carlotta Giacobbe¹, Dubravka Sisak-Jung², Andrew Fitch¹

1. European Synchrotron Radiation Facility, Grenoble, France 2. Dectris, Baden, Switzerland

email: catherine.dejoie@esrf.fr

The high-resolution powder diffraction beamline at ESRF (ID22), built with a dual-undulator source on the 6 GeV storage ring, combines a wide continuous range of incident energy (6-80 keV) with high brightness, offering the possibility to carry out high-flux, high-resolution powder diffraction measurements above 30 keV. In routine operation, a bank of nine scintillation detectors is scanned vertically to measure the diffracted intensity as a function of 2θ , each detector being preceded by a Si 111 analyzer crystal. The current detector system has operated successfully for the past 20 years. Nevertheless developments in detector technology can be exploited to improve the overall performance. In particular, at low diffraction angle, the axial acceptance of the detectors results in broadened and asymmetric peaks owing to the curvature of the Debye-Scherrer cones. At high diffraction angles, detection efficiency could be improved by up to an order of magnitude by increasing the axial acceptance of the detectors as the scattering power of the sample falls off naturally. In order to improve the detection efficiency behind the 9 analyzer crystals, a Pilatus3 X CdTe 300K-W was mounted on the arm of the diffractometer, and used for standard continuous-scanning acquisition on several test samples (Si, LaB6, ceria, ZSM-5 zeolite). By using a small area detector, the axial aperture can be varied with 2θ , narrow at low angles where the curvature is most marked, and wider at higher angles, where the curvature is less. In this way, as well as increasing overall counting efficiency, resolution and peak shapes at low angle are improved as compared to the current fixed, 4-mm-wide receiving aperture. In addition, by carefully selecting the diffraction region on the 2D images, parasitic signals can be avoided. Combining the high efficiency of a hybrid photon-counting area detector with the high resolution given by analyzer crystals is an effective approach to improving the overall performance of high resolution powder diffraction.

Keywords: high-resolution X-ray powder diffraction, Pilatus detector

MS20-O4

Synchrotron single-crystal diffraction for chemistry and materials: new developments

William Clegg1

 Chemistry, School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne, United Kingdom

email: bill.clegg@ncl.ac.uk

Prior to the 1990s there were no dedicated single-crystal diffraction beamlines for use by chemists and materials scientists; limited access was available to multi-purpose beamlines used also, and in most cases predominantly, for powder diffraction and/or spectroscopic techniques, along with some minor use of macromolecular crystallography beamlines. The design, construction, and commissioning of Station 9.8 at Daresbury Laboratory's Synchrotron Radiation Source (SRS)1 thus began what is now a rich though still brief 20-year history of bringing the advantages of synchrotron radiation to the community of chemical crystallographers familiar with this key technique in a standard local laboratory setting. The advantages derive from the special properties of synchrotron radiation, principally its high intensity, excellent collimation, and available range of wavelengths.

While the UK led the way, initially at SRS with Station 9.8 and its later more modestly configured Station 16.2SMX, the rapid uptake and exploitation of the new opportunities prompted similar development of dedicated and optimised single-crystal diffraction beamlines elsewhere, notably at ALS, together with enhancement of single-crystal diffraction facilities on shared beamlines such as those at ESRF, APS, and Soleil. With the closure of SRS, a new UK beamline (119) was designed and constructed at Diamond Light Source (DLS), beginning operation in 2008. This has recently undergone a major upgrade.²

These beamlines have been used for structural studies across all branches of organic, inorganic, materials, and pharmaceutical chemistry, and have played a vital role in the investigation of large-scale supramolecular assemblies and extended framework structures, with applications in gas and energy storage among other important modern research areas.

Our own use has included the elucidation of structures displayed on journal front covers, some unusual structural features such as highly strained metallated aromatic molecules, and a natural product with exceptional antibiotic properties. Recent achievements include the successful development of remote access operation of DLS beamline 119,³ which should now become the standard form of usage of the beamline, bringing many advantages. Examples will be shown, along with a summary of the history and new aspects.

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Keywords: Synchrotron, remote access, data collection



Total Scattering at the X04SA beamline of SLS

Antonio cervellino1, Ruggero Frison2

1. Photon Science Division, Villigen, Switzerland

2. Department of Chemistry, University of Zurich, Switzerland & Excelsus Structural Solutions (Swiss AG), PARK innovAARE, Switzerland, Zurich, Switzerland

email: antonio.cervellino@psi.ch

The X04SA Powder Diffraction beamline [1] has been developed with Total Scattering (TS) experiments at the forefront. The requirements for TS are perfectly compatible with maintaining the best capabilities for classical synchrotron XRPD, as the main TS requirement is - top data quality. The energy flexibility of the beamline (5 - 30 keV with)high photon flux and sufficient detection efficiency) and the excellent detectors installed (a 2D Pilatus 6M and a large 1-D Mythen II) make up the rest, allowing for the required momentum transfer especially with the Mythen II [1]. In fact, collecting data to 140 deg with the Mythen, the Qmax can reach > 28 Å-1, sufficient for most materials, while especial emphasis is given to reciprocal space TS (modelling the data directly from atomic coordinates via the Debye Scattering Equation, as per the DFA method [2]), where the absence of a direct Fourier transform of the data makes the need for high Qmax less stringent whilst the data quality must be even higher in all respects.

Increasing data quality is a process that involves the hardware – whereas all forms of parasitic scattering and all instrumental and intrinsic distortions (inelastic scattering, absorption,..) can be minimised and/or corrected whilst maximizing the sample scattering signal. The software plays also a critical role, inasmuch the information content of the data is fully preserved and the raw data are processed, corrected and subtracted [2] to yield precisely the desired part – the sample's elastic scattering pattern and its absolute scale sharpened counterpart S(Q) or the latter's direct space Fourier equivalent interatomic distance pair distribution function G(r).

The hardware (rotating capillary, liquid jet and suspended droplet) enhancements will be presented, together with the state-of-the-art, never before presented procedures and algorithms for calibrating the detector (pixel-wise positional and efficiency corrections [2]) together with the most effective and still partly unpublished algorithms and methods for data processing, merging, subtraction and correction – including a novel lossless smoothing-denoising [2] that permits to acquire high-quality low-noise background patterns in a fraction of the time previously required. Furthermore, subsequent processing [2] to obtain the absolute scale sharpened S(Q) and the G(r) functions in a reliable and automated way are presented and compared with existing dedicated softwares like (GudrunX [3], PdtGetX3 [3].

As an outlook, simultaneous Quantitative Phase Analysis in Q and r spaces – thus made independent from the crystallinity of components - is envisaged. References:

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Keywords: Synchrotron XRPD, Total Scattering, Data processing

MS21 Intermolecular interactions from structural, energetic and charge density perspective(s)

Chairs: Prof. Enrique Espinosa, Prof. Ulli Englert

MS21-01

Stay hydrated – where pharmaceutical hydrates come from and why

Katharina Edkins¹

1. School of Pharmacy, Queen's University Belfast, Belfast, United Kingdom

email: k.edkins@qub.ac.uk

Multiple crystal forms in pharmaceuticals pose severe risks to the formulation of a novel medicine, and to its safety and efficacy. In particular, the inclusion of water into the crystal lattice and thus the formation of crystalline hydrates generates challenging materials for formulation due to their thermodynamic low water solubility. Variations in hydrate stability in addition to the existence of stoichiometric and non-stoichiometric behaviour pose additional problems, which require non-trivial solutions. It is thus a major area of interest in the pharmaceutical industry to discover hydrated crystal forms and avoid them if possible.

The classic approach of hydrate research is the solvent screening of a compound to explore the crystallisation space and detect as many crystal forms as experimentally accessible, which are then analysed in detail.1,2 Whilst this approach gives detailed insight into the stability of the chosen crystal form and can explain their solid-state behaviour, it is a retrospect approach in which the hydrate must be found before it can be analysed. We are interested in interactions being present in solution before crystallisation and their connection to the resulting crystal form with the aim to predict hydrate formation before conducting the crystallisation experiment. The use of spectroscopic methods in combination with neutron scattering and simulation proves particularly powerful, and this approach will be presented using several well-known drug compounds ranging in their hydrate stability and water solubility.

Keywords: Hydrogen bonding, crystal form, pre-nucleation aggregates

MS21-O2

Chemical insights from systematic studies of interactions in re...

Simon Colest

1. Chemistry, University of Southampton, Southampton, United Kingdom

email: s.j.coles@soton.ac.uk

Many industries, most notably pharmaceutical, have for some time been using compound libraries as a systematic approach to comprehensively understanding a chemical landscape. Screening in medicinal chemistry is an obvious example and QSAR takes a similar, in-silico, approach. Understanding packing and structure-determining factors in the solid state is key in many areas eg polymorphism or crystallization, and of course we need to understand this behaviour if we are to control solid-state formation in any way. Our research uses systematic studies on the crystal structures of homologous series of compounds to derive rules and begin to predict solid-state behaviour. We now extend this concept to the application of Quantum Crystallography approaches to series of compounds in order to further understanding of structure and properties.

The talk will present examples of series of compounds specifically designed to examine:

- 1. Transition states for N-C bond formation;
- 2. Tuning receptor structure to optimise anion binding;
- 3. Co-former selection for pharmaceutical co-crystals;
- 4. Rationalising properties of co-crystals;
- 5. The role of fluorine interactions in the organic solid state;
- Tailoring aromatic intermolecular interactions to activate spin-crossover materials.

In all of the above, a deep understanding of the complementary and competitive energetic contributions is necessary in order to rationalise solid-state structures and their behaviour.

Keywords: Quantum Crystallography, Structural Systematics

MS21-O3

Polarizing multipolar atoms: a new toolbox for benchmarking and more

Théo Leduc¹, Emmanuel Aubert¹, Christian Jelsch¹, Cristian Iordache¹, Enrique Espinosa¹, Benoit Guillot¹

1. CRM2, Université de Lorraine, Nancy, France

email: theo.leduc@univ-lorraine.fr

Ab initio calculations are becoming applicable on larger and larger molecules; nevertheless designing models of lower complexity is not devoid of interest for modeling biological complexes. Compared to point charge/moment models, electron density models add a rich layer of information: atomic basins, bond topology descriptors, etc. This study aims to improve electrostatic interaction energy calculations based on transferable multipolar atoms [1] with explicit consideration of dipole induction. We focus on polarizability calculations on isolated and interacting molecules taken from a high-quality theoretical benchmarking dataset, for which a detailed energy partition scheme is available [2]. Since polarizabilities change upon binding, transferability of this physical quantity between similar atoms is in question. To assess this problem, the interplay of theoretical polarizability variations with molecular geometry, external electric fields and interaction energies have been carefully examined. We will present our preliminary results along with the new tools we implemented in MoProSuite [3] for this study.

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Keywords: Polarizabilities, Dipole, Transferability

MS21-O4

The role of the crystal field to determine hydrogen atom positions in strong intramolecular hydrogen bonds

Lorraine Andrade Malaspina¹, Sajesh P. Thomas², Kunihisa Sugimoto³, Simon Grabowsky¹

- 1. Institute of Inorganic Chemistry and Crystallography, University of Bremen, Bremen, Germany
- 2. Department of Chemistry, Aarhus University, Aarhus, Denmark
- 3. Japan Synchrotron Radiation Research Institute (JASRI), Hyogo, Japan

email: lorraine.malaspina@gmail.com

The hydrogen maleate (HM) anion (Figure 1) has been investigated extensively in the past due to its very short intramolecular hydrogen bond. This hydrogen bond closes the HM anion to a seven-membered ring configuration in a resonance-assisted hydrogen bond (RAHB) fashion.[1]

There is a large number of crystal structures of hydrogen maleate salts in the Cambridge Structural Database (CSD) which show that the O···O distance varies from 2.361 to 2.540 Å with a large variety of intermediate distances, with the hydrogen bond varying from perfectly symmetric to highly asymmetric. Neutron-diffraction experiments have shown that the proton position is highly dependent on the counter cation and hence on the intermolecular interaction pattern, exemplifying the flexibility of this compound regarding intermolecular interactions and crystalline environments.[1]

The crystalline environment polarizes the two oxygen atoms O1 and O2 to different extents. The bigger the difference in the polarization of the two oxygen atoms, the higher the asymmetry in the hydrogen atom position of the intramolecular RAHB. Consequently, hydrogen atom H1 shifts more closely to the oxygen atom that is less polarized by the environment. The asymmetry of the RAHB is therefore in direct relationship with the asymmetry of the intermolecular interaction pattern and the crystalline environment.

In this work the trajectory of the proton transfer is mapped through experimental electron density (ED) studies of a series of HM salts (cations: 4-aminopyridinium, 8-hydroxyquinolinium, K, Mg, Ca, Li, Na) using high-resolution low-temperature synchrotron X-ray diffraction data measured at the beamline BL02B1 of SPring-8, Japan. The experimental electron density was modeled using the Hansen–Coppens multipole formalism,[2] and X-ray wavefunction refinement [3]. The response of the hydrogen atom position to the experimentally derived electric field imposed by the crystallographic environment will be presented and discussed. Changes in the character of the O-H...O bond will furthermore be characterized utilizing a complementary bonding analysis based on quantum crystallography.



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Keywords: Experimental electron density, electric field, crystalline environment

MS21-O5

Quantum crystallography towards "quantitative crystal engineering"

Sajesh P Thomas¹, Peter R. Spackman², Khidhir Alhameedi², Dylan Jayatilaka², Bo B. Iversen¹, Mark A. Spackman²

- 1. Department of Chemistry, Aarhus 8000, Denmark
- 2. School of Molecular Sciences, The University of Western Australia, Perth, Australia

email: sajeshpthomas@gmail.com

Understanding solid-state supramolecular chemistry requires quantitative insights into the nature and strength of intermolecular interactions. Over the past few decades, charge density multipole modelling (CDMM) formalism has contributed significantly to the understanding of chemical bonding in crystals [1]. However, the applicability and accuracy of CDMM in the intermolecular regime is a grey area. This is owing to the issues related to the partitioning of electron density in the intermolecular space using CDMM. Recent developments in the high resolution X-ray quantum crystallography offer significant prospects in this context. I will discuss recent results on the studies of intermolecular interactions, their strength and nature in terms of bond orders, electron density and interaction energies derived from both experiment and theory. Especially the applications of such quantitative descriptors will be discussed in the context of crystal engineering of molecular solids, their relative stabilities and intriguing mechanical properties[2,3].

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Keywords: charge density, crystal engineering, intermolecular interactions

MS22 Molecular structure and chemical properties: chemistry meets charge density

Chairs: Dr. Vladimir Stilinovic, Dr. Jacob Overgaard

MS22-O1

Benchmarking lithium amide versus amine bonding by charge density and energy decomposition analysis arguments

Dietmar Prof. Dr. Stalke1,

1. Institute of Inorganic Chemistry, Goettingen, Germany

email: dstalke@chemie.uni-goettingen.de

First, lithium amides are versatile C-H metallation reagents of vast industrial demand because of their high basicity combined with weak nucleophilicity, [1] applied worldwide annually in kilotons. Second, bonding is the most basic concept in chemistry, but there are no dashes known from the Lewis diagram in nature. Experimental charge density from high resolution diffraction data and topological analyses quantifies bonding beyond plane interatomic distances. Covalent, electrostatic and donating bonding are the three most widespread concepts. The computational energy decomposition analysis adds their energy contributions. With these two interlocked methods we revisited industrial important amine-donated lithium amides, quantified covalent Li–N, electrostatic Li⁻N⁻ and donating Li \leftarrow -N bonding and paved the way to modify their reactivity. [2]

Fig. 1 Partitioning of the interaction energy into the Pauli, dispersion, electrostatic and orbital terms gives a 71-72 % ionic and 25-26 % covalent character of the Li–N, different to the old dichotomy of 95 to 5 %. In this light, there is much more potential to steer reactivity with various substituents and donor solvents than anticipated so far. [3]



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Keywords: charge density, lithium amides, energy decomposition analysis

MS22-O2

Complementary bonding analyses based on quantum crystallography

Simon Grabowsky1, Malte Fugel1, Maksym V. Ponomarenko1

 University of Bremen, Department 2 - Biology/Chemistry, Institute of Inorganic Chemistry and Crystallography, Bremen, Germany

email: simon.grabowsky@uni-bremen.de

Extracting information about chemical bonding from a molecular wavefunction or an experimental electron density is an ambiguous task since the notion of a chemical bond is itself a fuzzy concept that is not measurable and can therefore not be defined rigidly. There are recent heated debates on fundamental terms such as donor-acceptor interactions,[1] hypervalency,[2] or bond paths [3] in the literature. Even the meaning of ionicity and covalency is under question.[4] However, no chemist would deny that the chemical bond is a useful concept.

We do not claim that we can solve the debates, or redefine chemical bonding. However, there are hardly any studies that attempt to compare the results from a large variety of bonding descriptors on a single set of compounds without focusing on a specific tool or favoring one. Moreover, there are no studies that can show a comparison of results from experimental and theoretical investigations using the same orbital, real-space and energy bonding descriptors. Therefore, we have embarked on a systematic comparison of modern bonding descriptors from those three realms (specifically: quantum theory of atoms in molecules, source function, electron localizability (ELI), natural bond orbitals, natural resonance theory, valence bond calculations, different types of energy decomposition analyses, bond orders etc.), and we derive them from high-level theoretical calculations as well as experimental refinements of X-ray diffraction data within the new field of quantum crystallography.

We will show case studies for oxides of second- and third-period elements, for oxyanions such as nitrate, sulfate, phosphate, perchlorate that are of fundamental importance for chemistry, and for pentacoordinated silicon compounds. The results shed new light on hypervalency, charge-shift bonding, and ionicity vs. covalency concepts.

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Keywords: chemical bonding, quantum crystallography

MS22-O3

Multicentric two-electron covalent bonding (pancake bonding) between semiquinone radicals determines bulk properties

Krešimir Molčanov¹, Christian Jelsch², Emmanuel Wenger², Zhongyu Mou³, Miklos Kertesz³, Bruno Landeros-Rivera⁴, Jesus Hernandez-Trujillo⁴, Vladimir Stilinović⁵, Biserka Kojić-Prodić¹

- Department of Physical Chemistry, Rudjer Bošković Institute, Zagreb, Croatia
- Cristallographie, Résonance Magnetique et Modélisations, UMR 7036, Institut Jean Barriol, CNRS and Université de Lorraine, Nancy, France
- 3. Georgetown University, Washington, United States of America
- 4. UNAM Mexico City, Mexico City, Mexico
- 5. Faculty of Science, University of Zagreb, Zagreb, Croatia

email: kmolcano@irb.hr

Fine details of stacking interactions in three different types of π -stacked tetrachlorosemiquinone radical anions (Cl_QQ) were studied by a combination of X-ray charge density, quantum chemical computation and atoms-in-molecules (AIM) analysis: 1) stacks of pancake-bonded radical dimers in triclinic polymorph of *N*-MePy-Cl₄Q (*N*-MePy = *N*-methylpyridinium cation), 2) stacks of trimers of partially charged semiquinones in [4-damp]₂[Cl₄Q]₃ (4-damp = 4-dimethylamino-*N*-methylpyridinium) and 3) stacks of equidistant radicals in orthorhombic polymorph of *N*-MePy-Cl₄Q. For the first time, we provide experimental evidence (based on X-ray charge density) of two-electron multicentric covalent bonding (pancake bonding) between the radicals.

Typical pancake-bonded radical dimers in 1) are characterised by short interplanar distance (2.86 Å) and multiple bonding (3,-1) critical points between the rings with maximum electron density exceeding 0.095 e Å⁻³; in addition, a (3,+3) critical point (local minimum of electron density) was also found, indicating a cage-like electronic structure. The covalent contribution to total interaction in a dimer was calculated to be -9.4 kcal mol⁻¹. Between the dimers, interplanar separation is 3.60 Å and only negligible electron density is found.

In trimers there are two electrons shared between three closely interacting rings (interplanar separations are *ca.* 2.84 Å), and (3,-1) bonding critical points are found with maximum electron density of 0.077 e Å⁻³; there are also two (3,+3) local minima [1]. The calculated covalent contribution is -6.8 kcal mol⁻¹

Maximum electron density between the rings in a stack of equidistant radicals (interplanar separation of 3.17 Å) is much lower, 0.050 e Å⁻³, and there is no local minimum of electron density. However, the HOMO orbitals extend between the rings, and the calculated covalent contribution is -2.9 kcal mol⁻¹. This compound is a 1D semiconductor [2,3], and its semiconductivity is explained by pancake bonding extending along the stack.

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Keywords: semiquinones, two-electron multicentric bonding, stacking

MS22-O4

Investigating short strong hydrogen bonds (SSHBs) with potential proton migration behaviour using experimental charge density analysis

Lucy Saunders1, Chris Frampton2, Harriott Nowell1, Dave Allan1

- 1. I19, Diamond Light Source, Didcot, United Kingdom
- 2. Wolfson Centre for Materials Chemistry, Brunel University London, Uxbridge, United Kingdom

email: lucy.saunders@diamond.ac.uk

Proton migration involves a gradual shift in hydrogen atom position across a hydrogen bond (HB). In the solid-state, this behaviour may occur as a function of an external variable including temperature¹ or pressure.² Such behaviour is typically observed in HBs characterised by very short donor-acceptor distances (short strong hydrogen bonds – SSHBs), in the range of 2.5 Å for O—H···O HBs¹ and 2.6 Å for N—H···O HBs,⁴ where the barrier to proton transfer is low.⁵

Potentially useful solid-state physical properties including ferroelectrics⁶ or thermochromism² may result following proton migration across SSHBs. Increasing the understanding of where such behaviour is manifest may allow functional materials to be accessed more reliably in future; correlations to donor-acceptor distances and $\Delta p K_a$ values of components have previously been made.⁸

In this work, we present variable temperature single crystal synchrotron X-ray diffraction (SCSXRD) studies of several potential proton migration materials. These materials are multi-component organic co-crystals/salts (carboxylic acids with urea/N-heterocycle co-formers) where SSHBs form the connections between molecules. For the most promising migration materials, we use experimental charge density analvsis to investigate the SSHBs across which this behaviour is suggested and attempt to unravel the chemical bonding and/or molecular features that contribute. We present results from multipolar refinements (performed in XD200610 using Hansen and Coppens formulism11) of charge density data collected on beamline I19, Diamond Light Source (UK).⁹ We also discuss aspects of the data collection strategy implemented to obtain the quality high resolution data required for the charge density analysis.

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MS22-O5

Dynamic quantum crystallography

Anders Østergaard Madsen¹, Anna Hoser², Ioana Sovago³

- 1. Department of Pharmacy, University of Copenhagen, Copenhagen, Denmark
- 2. Department of Chemistry, University of Warsaw, Warsaw, Poland
- 3. Department of Chemistry, University of Copenhagen, Copenhagen, Denmark

email: a.madsen@sund.ku.dk

From the point of view of X-ray scattering the electron density and the nuclear density are communicating vessels, and it is important to model both in order to get a full picture of the charge density. We use quantum mechanics to construct models of the thermal vibrations in crystals, which can be refined and/or validated against scattering data. Scattering data is here understood in the broadest sense; the traditional methods of X-ray and neutron diffraction could be complemented by other probes, such as ssNMR, Raman and terahertz spectroscopies, as well as inelastic scattering or thermal diffuse scattering, which are all techniques that holds the key to understand the correlated motion of atoms in crystals. The use of quantum mechanics in crystallography has a long history, however in most applications the quantum mechanical modeling has focused on the description of the electron density. Much less attention has been devoted to the nuclear motion, although the atoms in the crystal are of course vibrating, even at the lowest temperatures. This is unfortunate. Not only does the atomic and molecular motion define important physico-chemical properties such as the mechanical and thermodynamic stability of the crystal, but the concerted motion of atoms give rise to thermal diffuse scattering which affects the Bragg intensities. Ultimately, the quantum-mechanical models of electron density distribution and nuclear motion should amalgamate into a common model, which can be compared and refined against the experimental evidence, and which can be used to understand solid state properties at the atomic level. We will present our recent approach to refine lattice-dynamical models against diffraction data [1,2], demonstrate a combined model of normal mode and multipole refinement [3], and give examples of how the dynamics derived from these models can be used to derive heat capacities and free energies in order to investigate the relative stability of polymorphic molecular systems.

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Keywords: Quantum Crystallography, Lattice dynamics, charge densities

MS23 Advances in electron crystallography methods

Chairs: Dr. Mariana Klementova, Dr. Enrico Mugaioli

MS23-O1

Characterising the strain in a twisted nanowire by scanning electron diffraction

Alexander Eggeman¹, Daniel Ugarte², Monica Cotta², Luiz Tizei³, Caterina Ducati⁴, Paul Midgley⁴

- School of Materials, University of Manchester, Manchester, United Kingdom
- Instituto de Fisica, Universidade Estadual de Campias, Campinas, Brazil
- 3. Laboratoire de Physique des Solides, Universite Paris Sud, Paris, France
- Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom

email: alexander.eggeman@manchester.ac.uk

Transmission electron microscopes offer the capability to study materials using a variety of signals at extremely high spatial resolution and with high precision. This combination is essential when considering nanoscale materials as the variations in structure and composition can occur over very short legth-scales and can have profound impact on the properties and hence the function of the material.

Here we present a detailed analysis of structural distortions present in a hexagonal indium phosphide nanowire containing a screw dislocation [1]. The wire exhibits strain varying radially from the dislocation core outwards but the free surface of the wire also results in a back torsion (the classical Eshelby twist [2]) causing a continuous twist of the crystal structure along the length of the wire. From a series of scanning precession electron diffraction [3] measurements the twist rate and the radial strain have been characterised in great detail and found to be consistent with a common Burger's vector of the hexagonal c-axis value. Validation of this analysis was performed using dynamical scattering simulations of a model twisted nanowire. In addition, information about the growth direction, dislocation handedness and even the 3D wire morphology could be extracted from the measurements.

This study highlights many of the advantages as well as some of the limitations of scanning precession electron diffraction data for studying nanomaterials.



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Keywords: Precession, Nanowire,

MS23-O2

Electron tomography of radiation sensitive 3D nano-crystals in imaging and diffraction mode

Jan Pieter Abrahams¹, Max Clabbers², Eric van Genderen³, Thorsten Blum³

- 1. C-CINA, Basel University and LNB, Paul Scherrer Institute, Basel and Villigen, Switzerland
- 2. C-CINA, Basel University, Basel, Switzerland
- 3. LNB, Paul Scherrer Institute, Villigen, Switzerland

email: Jan-Pieter.Abrahams@psi.ch

Any electron microscope allows collecting electron diffraction data both in diffraction and in imaging mode. Both modes have their strengths and weaknesses. The advantage of electron imaging is that it provides spatial phase information of the sample, but at the expense of contrast. The advantage of electron diffraction is that it provides high contrast, but at the expense of spatial phase information. Here, we discuss how to exploit the strengths of both methods and how to combine them, in order to infer all the required information of radiation sensitive samples.

We show that by collecting in diffraction, we can measure up to 1000 times more useful data of weakly scattering, organic material, compared to imaging mode. We explain this significant difference from first principles and show that it is an intrisic limitation of imaging. Thus, we can explain why it is possible to collect a full three-dimensional high-resolution electron diffraction data set of a single protein nano-crystal, with the same number of electrons that is required for just a single high-resolution image of the same crystal.

Diffraction data lacks spatial phase information. Such information can be inferred from prior information of the sample, but when this is not available, it needs to be measered experimentally. One way of measuring spatial phases in three dimensions, is by electron tomography in imaging mode. Although wasteful in terms of electron dose (and hence causing increased radiation damage), it does provide independent phase information. We discuss recent results.

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Keywords: Electron diffraction, protein crystallography, electron tomography

MS23-O3

Low-dose scanning electron diffraction and pharmaceutical nanostructure

Duncan Johnstone¹, Christopher S. Allen², Mohsen Danaie², Royston C.B. Copley³, Anais Lafontaine⁴, Jeffrey Brum³, Angus I. Kirkland², Paul A. Midgley⁴

- 1. Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom
- Electron Physical Sciences Imaging Centre (ePSIC), Diamond Light Source Ltd & Department of Materials, University of Oxford, Oxford, United Kingdom
- Physical Properties, Analytical Sciences and Development, GlaxoSmithKline Pharmaceuticals, Stevenage, United Kingdom
- 4. Evreux Materials Science, GlaxoSmithKline, Evreux, France

email: dnj23@cam.ac.uk

The active ingredients and excipients formulated together in pharmaceutical products are often organic crystals. Whilst X-ray diffraction is ideal for probing the atomic structure of these organic crystals, it has limited use in investigating any heterogeneity of the pharmaceutical at the nanoscale [1]. Such 'nanostructure' may affect product performance and can, in principle, be probed by transmission electron microscopy but, until recently, beam damage has proven to be a major limiting factor [1]. Scanning electron diffraction (SED) is a new approach to acquiring nanoscale data from beam-sensitive materials [2,3]. SED involves the acquisition of a two-dimensional electron diffraction pattern at every probe position as a nm-sized electron probe is scanned across the specimen. If each pattern can be acquired before significant structural degradation (typically a few ms), the 4D-SED dataset contains a wealth of nanoscale crystallographic data, making the technique a highly versatile hybrid diffraction-imaging approach.

Here, we report on the development of low-dose SED, in which diffraction patterns from pharmaceutical organic solids were recorded with an electron fluence of ~ 5 e/Å² and a spatial resolution of ~ 5 nm. Such low dose acquisition is greatly enhanced by the use of direct electron detectors and represents a reduction of approximately 2 orders of magnitude compared to previous SED of soft materials [2,3]. In particular, we used the Merlin-medipix detector system, a counting type detector, particularly suited to this kind of diffraction pattern acquisition owing to essentially zero noise acquisition and high dynamic range. A probe current of 1.6 pA and a dwell time of 1 ms per probe position was used in the SED acquisition. A highly parallel (~0.6 mrad convergence angle) beam was used and a reciprocal space structural resolution of better than 1 Å⁻¹ was obtained.

Results will be presented from a number of off the shelf active pharmaceutical ingredients, namely bicalutamide, acetaminophen, and probucol, as well as excipients lactose monohydrate and magnesium stearate. These materials span a range of reported characteristic doses and SED data were successfully obtained in all cases. For the most beam sensitive materials, the acquisition protocol is such that repeated scanning of the same area reveals almost complete destruction of the crystallinity – i.e. a 'diffract and destroy' approach. Nevertheless, high-quality diffraction data are obtained. Therefore, low-dose SED, as developed in this work, provides an essential platform for the investigation of nanostructure in pharmaceutical materials and other organic solids.

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Keywords: scanning electron diffraction, pharmaceuticals, nanostructure

MS23-O4

Possibility of improved phasing method on Micro-ED

Tsumoru Shintake1, Cathal Cassidy1

 OIST: Okinawa Institute Science and Technology, Graduate University, 1919-1 Tancha, Onna, Okinawa 904-0495, Japan

email: shintake@oist.jp

The author discuss on basic physics of Bragg diffractions, and introduce a new way of image capturing on Bragg diffractions instead of Fraunhofer diffractions in a transmission electron microscope. There is a possibility to improve the phasing process on the protein crystallography (Micro-ED). In this scheme, we do not require standard phasing techniques; such as Multi-wavelength Anomalous Diffraction (MAD) method used in X-ray crystallography. The author also discuss on limitations on this scheme.

Keywords: Micro-ED, Phasing

MS23-05

Automated diffraction tomography in TEM and STEM mode – getting the best of both worlds

Ute Kolb1, Sergi Plana-Ruiz2, Yasar Krysiak1, Haishuang Zhao1

1. Johannes Gutenberg University Mainz, Mainz, Germany

2. Universitat de Barcelona, Barcelona, Spain

email: kolb@uni-mainz.de

In the last decade electron crystallography experienced a boost through the development of electron diffraction tomography. After data acquisition and processing strategies were developed for automated diffraction tomography [1] a big range of methods has been set up in order to improve the collection of data in reciprocal space. A major difference between the methods is the crystal tracking strategy carried out in TEM or STEM mode. While the use of TEM for electron diffraction tomography methods allows the application of both, selected area or nano-beam diffraction, the STEM mode will only facilitate the later. Both data collection approaches already proved successful for structure solution and refinement using single nano- sized crystals. Significant differences appear for example if the size of crystalline domains are in the regime of some tens of nanometer or the material is highly beam sensitive. The use of a small condenser aperture (10 µm) to produce a quasi-parallel electron probe allows the access of these materials as a nanometer-beam (2-10 nm) with low convergence angle (0.4-1 mrad) reduces the electron dose using dark-field detectors for crystal imaging in scanning mode [2]. Automated diffraction tomography utilizes in addition the advantage that only a slight change of focus allows to switch between imaging and diffraction conditions [2]. In order to obtain improved electron diffraction data electron beam precession using this beam configuration is added. This allows electron diffraction data acquisition with expanded number of excited spots and with further minimized dynamical effects suitable for crystal structure refinement using kinematical and dynamical approach. For the above described data collection strategy it is necessary to obtain an accurate alignment of such a beam setting, which may not be available as a default implemented option in a TEM. Thus a general method to set illuminating conditions for selectable beam convergence and probe size has been works out for Transmission Electron Microscopes (TEM) fitted with µs/pixel fast beam scanning control, (S)TEM, and an annular dark field detector [3]. Additionally, scripts for different TEM platforms addressing the above described data collection strategies were developed.

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S.Nicolopoulos, (2018) Ultramicroscopy, 193, 39-51

Keywords: electron diffraction tomography, scanning transmission electron microscopy, structure solution

MS24 Defects and disorder quantification at the nanoscale

Chairs: Dr. Partha Pratim Das, Dr. Tatiana Gorelik

MS24-01

Defects, disorder and electrochemistry in layered metal-ion battery cathodes

Artem Abakumov¹

1. Center for Electrochemical Energy Storage, Skolkovo Institute of Science and Technology, Moscow, Russia

email: a.abakumov@skoltech.ru

Layered rock-salt-type oxides A1+xM1-xO2 (A - alkali cation, M - transition metal cation) are among the most promising positive electrode (cathode) materials for metal-ion batteries, offering specific capacity up to 250 mAh/g. The parent structure of the A_{1+x}M_{1-x}O₂ oxides is based on "cubic" close packing of oxygen atoms where the A and M cations occupy octahedral interstices in an ordered manner forming alternating layers. On a local scale, however, the structure of these materials is much more complex, featuring different kinds of defects and partial disorder, related to fractional occupation of the octahedral positon in the M layers with the excessive A cations (x > 0) with subsequent A/M ordering, antisite A/M disorder, stacking faults in the A/M ordered layers and twinning of the close packed layers. Electrochemical extraction of the A cations introduces intricate evolution of the defect structure, related to gliding of the close packed layers with respect to each other, partially reversible migration of the M cations to the vacant positions in the A-layers with subsequent ordering to a spinel-type structure, trapping of the M cations in the tetrahedral interstices, anion vacancies due to oxygen loss at high potentials and surface structure "densification" due to the oxygen loss or even a conversion to a framework structures. The defect structure of the pristine, charged, discharged and cycled A1+xM1-xO2 materials will be demonstrated using aberration-corrected scanning transmission electron microscopy and correlated with the peculiarities of their electrochemical behavior, such as operating potential, capacity and voltage fade [1-3].



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Keywords: electron microscopy, defects, metal-ion batteries

MS24-O2

Single crystal diffuse scattering for analyzing structures of dilute defects

Arkadiy Simonov¹

1. Crystallography, University of Freiburg, Freiburg, Germany

email: arkadiy.simonov@krist.uni-freiburg.de

With the recent advances in synchrotrons and area detectors, high quality single crystal diffuse scattering datasets can be routinely measured in a matter of minutes. However, analysis of diffuse scattering is still a bottleneck. It often requires construction of multiple test models and complicated refinements, and typically takes months of work and tens of thousands of computer hours.

Recently it was shown that in favourable cases of translational disorder diffuse scattering can be analyzed analogous to the Bragg peaks[1]. In such cases diffuse scattering can be used as a 'virtual structure factor', which can be combined with conventional structure factor to improve the resolution of refined atomic structure.

In the present contribution we extend this approach to the case of crystals with dilute defects. We show how information about defect distribution can be deconvolved from the virtual structure factor, and how the structure of defect can be found from diffuse scattering alone, without the use of Bragg peaks.

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Keywords: Diffuse scattering, defects, disorder, phasing

MS24-O3

Investigation of planar defects in electrode materials using FAULTS

Marine Reynaud¹, Jon Serrano-Sevillano¹, Amaia Saracibar², Thomas Altantzis³, Sara Bals³, Gustaaf van Tendeloo³, Jokin Rikarte¹, Juan Rodríguez-Carvajal⁴, Montse Casas-Cabanas¹

- Solid State Electroactive Materials Group CIC energiGUNE, Vitoria-Gasteiz , Spain
- Physical Chemistry Department, Basque Country University, Pharmacy Faculty, Vitoria-Gasteiz, Spain
- Electron Microscopy for Materials Research (EMAT), University of Antwerp, Antwerp, Belgium
- 4. Diffraction group Institut Laue Langevin, Grenoble, France

email: mreynaud@cicenergigune.com

The physical-chemical properties of functional materials are directly related to their structural features, and this is particularly relevant in the field of electrochemical energy storage. The thorough microstructural characterization of these materials, which includes the determination of different kinds of defects, their amount and their locations, is therefore of high importance.

Most Rietveld refinement programs include microstructural models that enable to extract valuable information regarding microstructural features such as point defects, finite crystallite size, microstrains or antiphase domains. All these features have a strong impact on materials' properties and are therefore essential variables for their complete understanding. However this approach faces several limitations in the case of crystalline materials with extended defects such as stacking faults, since they are poorly described with an average unit cell.

A different approach, using the recursive property of crystals, was used to develop the DIFFaX code, which allows simulating diffraction patterns of crystal systems with coherent planar defects [1]. Taking a step further, we have developed the FAULTS program from the core of DIFFaX so as to enable the refinement of experimental X-ray and Neutron powder diffraction patterns of faulted crystal systems [2]. An improved version of this program, more performant and with additional features is now available as an open program (www.cicenergigune.com/faults) and within the FullProf suite of programs (www.ill.eu/sites/fullprof).

Our presentation will show examples of several battery materials having different kinds of defects to illustrate how, besides classic structural determination, precise quantitative information regarding microstructural features such as stacking faults, twinning or intergrowths can now be extracted from diffraction data to establish correlations with materials' properties. Hence, using a simple layered description for the 3D framework of EMD-MnO₂, we performed the first quantitative analysis of ramsdellite motifs into a pyrolusite structure [2]. Another example refers to Li-rich layered oxides such as Li₂MnO₃, (also written Li[Li1/3Mn2/3]O2 to better account for its layered structure). These materials are known to crystallize with significant amounts of stacking faults, and we will show how the FAULTS program has allowed decoupling the individual role of crystallite size and amount of defects on the electrochemical properties of a series of samples of Li₂MnO₃ [3].

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 Serrano-Sevillano, J. et al. Submitted.

Keywords: powder diffraction, stacking faults, battery materials

MS24-O4

Topotactic transformations during thermolysis of Mg-Ga(Al) LDHs: structure of disordered nanocrystalline phases

Svetlana Cherepanova1, Nataliya Leonteva2

- 1. Novosibirsk State University, Novosibirsk, Russia
- 2. Institute of Hydrocarbons Processing, Omsk, Russia

email: svch@catalysis.ru

Layered double hydroxides (LDHs) have hydrotalcite structure, which consists of the Mg(OH)2-like layers formed by the closest packing of oxygen ions from OH groups. Octahedra are filled with divalent and trivalent cations. The latter create an excess positive charge compensated by the interlayer anions. The interlayer spaces also contain H2O. It was shown that initial carbonate-containing Mg-Ga (Mg:Ga=2-4) and Mg-Al (Mg:Al=2-4) LDH's structure represents the mixture of 3R1 (AC=CB=BA=...) and 2H1 (AC=CA=...) polytypes. At ~200°C Mg-Ga and Mg-Al LDHs loose water and form metastable dehydrated phases. It was shown that both dehydrated phases consist of 3R₂ (AC~BA~CB~...) and 1H (AC~AC~...) polytypes. So this topotactic reaction leads to the transformation of prismatic interlayers into octahedral ones that can be related to the change of orientation of CO32- anions. Calcination at ~400°C leads to the transformation of the dehydrated phases to the mixed Mg-Ga or Mg-Al oxides. It was shown that at low Mg content the mixed oxides consist of MgO-like octahedral layers and Mg-Al or Mg-Ga octahedral-tetrahedral spinel-like layers. MgO-like layers inherit the structure of Mg(OH)₂ ones; spinel-like layers are formed in the LDH interlayers due to diffusion of cations. TEM evidences that the oxide structure is 3D disordered. At high Mg contents the formation of partially inversed Mg-Al and Mg-Ga spinels along with layered oxides takes place. Rehydration of layered mixed oxides leads to the formation of three types of hydroxides having 1) hydrotalcite structure; 2) interstratified structure consisting of hydrotalcite and brucite layers; 3) brucite structure. The higher is Mg content, the lower is hydrotalcite structure reconstitution degree of rehydrated phase. Investigation of structures of initial, dehydrated, oxide and rehydrated phases was carried out with use of simulation of PXRD patterns on the basis of the models of 1D disordered structures of nanocrystalline materials with use of softwares [1] and [2]. PXRD patterns for 3D disordered layered mixed oxides were calculated with use of Debye scattering equation realised in self-developed program.

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Keywords: LDH thermal decomposition, disorder, PXRD pattern simulation

MS24-05

Unraveling 2D polymerization: A topochemical reaction studied via total scattering

Gregor Hofer¹, Florian Grieder², Martin Kroeger³, A. Dieter Schlueter², Thomas Weber¹

- 1. Department of Materials, X-Ray Platform D-MATL, Zurich, Switzerland
- 2. Department of Materials, Laboratory of Polymer Chemistry, Zurich, Switzerland
- 3. Department of Materials, Polymer Physics, Zurich, Switzerland

email: gregor.hofer@mat.ethz.ch

Recently, the concept of single-crystalline photo-dimerization has been extended to create two-dimensional (2D) networks in the single-crystalline state [1]. To obtain these novel 2D polymers, the monomer is crystallized in a layered arrangement and afterwards photo-irradiated. This causes continuous formation of covalent bonds between adjacent monomer molecules, resulting in a single crystal of 2D-polymer sheet stacks. Heat treatment reverses the bond formation and the original monomer crystal is recovered. Polymerization and depolymerization can be suspended at any time by removing the crystals from the triggering source, allowing for detailed ex-situ structural investigations of any intermediate state

The 2D polymer developed by Kory et al. [1] was studied to understand the propagation of 2D polymerization via single-crystal total X-ray scattering experiments. Measurements were done at several increasing and decreasing degrees of conversion. The average structure revealed, inter alia, a hysteresis in the lattice parameter evolution during the polymerization-depolymerization cycle. The most notably change is a phase transformation and abrupt decrease of the c-axis (Figure 1a) by almost 1 Å during depolymerization. The time-dependent conversion was analyzed with the Johnson-Avrami-Mehl-Kolmogorov equation and combined with Monte-Carlo simulations as well as observations from the average structures. These results revealed that polymerization propagation proceeds in a partially self-impeding fashion [2]. The real structure is studied in detail via the 3D-APDF method [3]. The measured three-dimensional diffuse scattering patterns and refined \triangle PDF maps are dominated by displacive disorder (Figure 1b), but substitutional disorder contributions from the partially polymerized monomer can be identified. This information is used to describe the molecular correlations and further quantify the propagation mechanism. Polymerization and depolymerization are associated with substantial molecular movements which do not break the crystal. Breaking is prevented by several strain compensation mechanisms within the crystal itself. For example, the incorporated solvent molecules act not only as buffers but also as lubricant in-between sheets. Identifying strain sources and how they are compensated is of importance to engineer structurally perfect sheets. Only these can be used in potential applications such as membranes.

Figure 1: (a) Changes of the *c*-axis during polymerization and depolymerization [2]. (b) 3D- Δ PDF refinement of the *uv*0.08 layer highlighting observed (dotted circle) and modeled (dashed circle) PDF densities associated with displacive disorder between neighboring molecules within the same layer. Image contrast modified for better visualization.



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Keywords: Total Scattering, 2D Materials, Phase Transformation

MS25 Combined approaches for the structure determination of new materials at the nanoscale

> Chairs: Prof. Artem Abakumov Prof. Radovan Cerny

MS25-01

Zeolite SSZ-70: new understanding of a successful catalytic material

Stef Smeets1

1. Department of Materials and Environmental Chemistry, Stockholm, Sweden

email: stef.smeets@mmk.su.se

Understanding the regular arrangement of atoms within the zeolite structure is key to why and how these materials function, and to improve on the characteristics that make them useful. However, most zeolites, and many other industrially and commercially important materials, are used and produced in polycrystalline form, and not suitable for standard single-crystal structure analysis. Therefore, we have been developing methodology to uncover and characterize zeolite framework structures using X-ray powder diffraction (XRPD) data, often by making use of information gleaned from complementary characterization methods such as electron microscopy (HRTEM), electron diffraction and/or MAS NMR. This will be demonstrated on the basis a recent example, the structure of calcined high-silica zeolite SSZ-70 [1].

The synthesis of the zeolite SSZ-70 was first reported over 10 years ago [2], but its structure proved to be difficult to characterize, because its framework structure is highly disordered. HRTEM images, synchrotron XRPD data, and DNP-enhanced 2D NMR spectra, each providing crucial and complementary insights, were used to probe different structural aspects of calcined SSZ-70, ranging from the long-range average structure (> 500 nm) to short-range stacking sequences (ca. 50 nm) to local atomic-level compositions and structures (< 1 nm). This combination is particularly well suited to the investigation of materials with complex partially disordered structures that cannot be resolved with conventional X-ray diffraction analysis alone. With these insights, the novel catalytic behavior of SSZ-70 can be better understood and opportunities for enhancement recognized.



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Keywords: disorder, polycrystalline materials, zeolites

MS25-O2

Atomic scale 3D characterisation of hetero-nanosystems: a dose-efficient fusion of imaging and analytical techniques in scanning transmission electron microscopy

Sandra Van Aert1,

1. EMAT - University of Antwerp, Antwerp, Belgium)

email: sandra.vanaert@uantwerpen.be

The properties of nanosystems are essentially determined by the positions of the atoms, their chemical nature and the bonding between them, but a fundamental understanding on the connection between the 3D structure and the properties at a local scale has been slow to emerge. Clearly, the rational design of nanomaterials with desired functional properties strongly depends on the availability of quantitative 3D characterisation techniques at the atomic scale. Aberration-corrected scanning transmission electron microscopy (STEM) has become a powerful technique for materials characterization of complex nanosystems. Recent progress in the development of quantitative methods allows us to extract structural and chemical information from experimental images in 2D as well as in 3D. In quantitative STEM, images are treated as datasets from which structure parameters are determined by comparison with image simulations or by using parameter estimation-based methods. In order to retrieve the 3D atomic structure, the use of scattering cross-sections to count atoms along the viewing direction has become a successful technique. Cross-sections define the total scattered intensity for each atomic column. Their high sensitivity in combination with a statistical analysis enables us to count atoms with single-atom sensitivity. These atom counts can be used to create an initial atomic model with which an energy minimization can be applied to obtain a relaxed 3D reconstruction of the nanoparticle. Recent progress enables us to extend atom-counting from homogeneous to heterogeneous materials. The introduction of several atomic elements into nanostructures can enhance properties such as stability, catalytic activity and electrical response. However, for mixed columns, all types of elements will contribute differently to the experimental scattering cross-sections, significantly complicating atom-counting as compared to monotype nanostructures. In order to extend atom-counting to heterogeneous materials, we introduced a physics-based atomic lensing model. This model is capable of predicting scattering cross-sections in terms of the 3D atomic arrangement creating new possibilities for unravelling the 3D composition. However, since scattering cross-sections depend on both sample composition and thickness, additional measurements are required to separate out those different contributions. In particular, energy dispersive X-ray spectroscopy combined with STEM imaging enables us to count the number of atoms in hetero-nanosystems without the need for prior knowledge. This multimodal approach can even be used to unravel small atomic number differences. Finally, new quantitative STEM strategies using a so-called fast pixelated detector will be shown enabling us to unravel thickness, composition, and even the oxidation state and 3D ordering of atoms.

Keywords: scanning transmission electron microscopy, quantitative structure characterisation, hetero-nanosystems

MS25-O3

Local structure and lithium diffusion pathways in nanostructured $Li_4Mn_2O_5$ rock-salt cathode probed

Maria Diaz-Lopez¹, Yves Joly¹, Claire V. Colin¹, Valerie Pralong², Pierre Bordet¹

Institut Néel CNRS, Grenoble, France
 Crismat Ensicaen, Caen, France

email: maria.diaz-lopez@neel.cnrs.fr

The full structural description of a complex nanostructured Li₄Mn₂O₅ high capacity cathode showing record reversible capacities superior to the state-of-the-art Li-Mn-O electrodes [1], was achieved for the first time by the combined study of Near-Edge X-ray Absorption Spectroscopy (XANES), Pair Distribution Function (PDF) analysis of neutron and X-ray total scattering data. An initial model was proposed based the knowledge of the average rocksalt structure and the octahedral coordination environment of manganese indicated by XANES performed at the Mn K-edge. A combined Reverse Monte Carlo (RMC) refinement of neutron and X-ray total scattering data shows that while the manganese framework remains cubic and well-ordered a high degree of disorder exists for both oxygen and lithium, which are displaced from their original rock-salt positions. The validity of the refined model was confirmed by the agreement between the XANES simulated spectra using FDMNES and the experiment. Additionally, we elucidated the unique and unusual 3D lithium diffusion pathway in nanocrystalline Li4 involving 5-coordinated lithium sites by bond valence energy landscape maps calculations.

The structural information revealed here [2] is essential for the understanding of nanostructured $Li_{4}Mn_{2}O_{5}$ performance as a cathode material and would have great implications on the design and development of future cathode materials based on $Li_{4}Mn_{2}O_{4}$.

Figure 1. Top left: XANES data at the Mn K-edge and simulations. Bottom left: schematic view of the RMC refinement approach performed in a box containing 21 000 atoms. The refinement constraints are given in dashed lines and the simultaneously modelled neutron and X-ray total scattering data in full lines. Right: refined data.



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 Diaz-Lopez et al. (2018). Submitted.

Keywords: Reverse Monte Carlo modelling, XANES, total scattering

MS25-O4

Structure solution of organic crystals by a global fit to the pair distribution function

Martin U. Schmid1, Dragica Prill1, Carina Schlesinger1,

 Institut fuer Anorganische und Analytische Chemie, Goethe-Univ., Max-von-Laue-Str. 7, 60438, Frankfurt am Main, Germany

email: m.schmidt@chemie.uni-frankfurt.de

Local structures in crystalline, nanocrystalline and amorphous organic compounds can be investigated using pair distribution functions (PDFs). For organic compounds, the experimental determination of the PDF curves is very similar to that of inorganic compounds. However, the fit of stuructural models to the PDF curve has rarely been done for organic compounds. In our previous research, the method developments for structure determination from PDF of organic compounds were successful with determination of molecular position and orientation starting from random values, and lattice parameters and space group given as an input.[1] For nanocrystalline compounds the space group and lattice parameters are typically unknown. Therefore, we developed a global procedure in which the lattice parameters, space group, molecular position and orientation are determined by a fit to PDF data^[2]. The calculations are carried out with TOPAS6^[3]. The optimisation initiates with a large set of random starting structures in various space groups. The space groups are chosen according to the space group frequency of the corresponding compound class, regarding the chemical class and the molecular symmetry. The optimisation of lattice parameters starts from random values within the sensible range. The ranges are automatically chosen depending on the size of the investigated molecule and space group in which the calculations are preformed. At the present stage of the development, the molecules are treated as rigid bodies (However, intramolecular degrees of freedom should not be a major problem, given the good functionalities provided by TOPAS). Barbituric Acid and other small organic molecules were chosen as an examples. Synchrotron powder patterns were recorded at the NSLS (Brookhaven, USA) with the wavelength of 0.18 Å. Results of the global fit to the PDF data will be shown.

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Keywords: organic compounds, pair distribution function, structure solution

MS25-O5

Pharmaceutical polymorph characterization by high resolution low loss EELS spectroscopy and electron diffraction tomography

Partha Pratim Das¹, Andrey Chuvilin², Alejandro Gomez Perez¹, Enrico Mugnaioli³, Mauro Gemmi³, Mihaela Pop⁴, Stavros Nicolopoulos¹

- 1. NanoMEGAS SPRL, Brussels, Belgium
- 2. CIC NANOGUNE, Donostia San Sebastian, Spain
- 3. Center for Nanotechnology Innovation@NEST, Pisa, Italy
- 4. TeraCrystal, Cluj-Napoca, Romania

email: partha@ecrystsolutions.com

Polymorphism is critically important in the pharmaceutical industry, as different polymorphic forms usually have different physical properties like solubility, bioavailability etc... Undesired polymorphic forms (usually as "trace" quantities) can co-exist with main polymorphic forms during the synthetic process. Standard diffraction based techniques like conventional powder X-ray diffraction or spectroscopic techniques like IR/Raman may fail to reliably identity and characterize them at nm scale. Transmission Electron Microscopy (TEM) technique has the capability to characterize nm size crystals. Recently, a study of several organic/pharmaceutical compounds was carried out using conventional EELS where it was established its utility for drug molecules characterization [1]. In this work we present high resolution (monochromated) EELS-low loss (2-40 eV) characterization of two different pharmaceutical drug molecules (Compound 1 & 2) (Titan 60-300 low base at 300 keV, monochromated, 0.2 eV energy resolution) Fig. 1 shows comparison of EELS low loss signature for the two pharmaceutical drug compound. While a plasmon peak at 23eV is almost identical for both compounds, a region at 3-9 eV shows clear differences in the spectra, which could be used as possible fingerprint of the phases. Alternatively, crystalline compounds can be characterized using 3D Electron Diffraction (ED) Tomography, where a series of electron diffraction patterns are recorded with a fixed tilt step around an arbitrary axis from a nanometer size crystal [2]. From this 3D diffraction pattern dataset, unit cell parameter and symmetry can be determined and the crystal structure can be solved using ED extracted intensities dataset. In this work we present structure solution of two important pharmaceuticals compounds (Compound 3 and 4) [3]. Low dose 3D diffraction tomography data was collected using 120 KeV Zeiss Libra Microscope and Timepix camera.



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Keywords: EELS, Diffraction Tomography, Pharmaceuticals

MS26 Aperiodic and modulated structures

Chairs: Prof. Sven Lidin, Prof. Alla Arakcheeva

MS26-O1

Phase transitions in organic-inorganic hybrids

Anna Gagor¹

 Institute of Low Temperatures and Structure Research PAS, Wrocław, Poland

email: a.gagor@int.pan.wroc.pl

The organic-inorganic hybrids from the halometallate family are explored as functional materials. Many of them crystallize in polar space groups exhibiting non-linear optical, piezoelectric and ferroelectric properties. The iodometallates stand out from other halide connections having useful optical properties like thermochromism and photochromism. The revival of the interest in these materials has vitally been boosted by the application of (CH₃NH₃)PbI₃ in III generation 'perovskite' solar cells [1].

Hybrids that bear Pb2+, Sn2+, Sn3+, Bi3+, Sb3+ halide units in combination with organic counter-ions exhibit tremendous structural diversity due to the variety of the anionic substructures that may be adopted. The basic units: MX₆ octahedrons or MX₅ square pyramids may form numerous discrete or polymeric connections including edge-sharing, vertex sharing, and face-sharing motifs. The poly-anionic structures depend on the size and symmetry of organic cations, quantity, and distribution of proton and donor centers, and the size of the halogen atoms. Depending on the cation symmetry, size and amount of the dipole moment and donor potential the cations are dynamically disordered. The change in the dynamic states of the cations entails changes in the symmetry generating phase transitions. The interplay between the short-range intermolecular forces, the flexibility of the anionic units and associated with them steric effects, as well as the thermally activated dynamic of cations may stand at the origin of the formation of complex structures, including modulated phases, and complex phase sequences.

In this contribution phase transitions in the ferroelectric (4-NH₂C₅H₄NH)SbCl₄ (4-APCA) and thermochromic (CH₃C₃N₂H₄)SbI₄ hybrids are presented. 4-APCA is modulated within three structural phases [2]. The incommensurately modulated phase is stable between 270 and 304 K. At 270 K, a lock-in phase transition is observed for the commensurate ferroelectric phase. Further cooling leads to commensurate-incommensurate transformation which is accompanied by the formation of a dense domain structure which disappears after the conversion to the low-temperature phase. The differences between the structures of the subsequent phases should be perceived as the mutual displacements of the anionic groups and rearrangements of 4-AP mediated by the hydrogen bonds. The crystals of (CH₃C₃N₂H₄)SbI₄ undergo a phase transition to incommensurately modulated phase around 295 K which is associated with a subtle distortion of [SbI4] n chains of edge-shared

octahedrons [3]. The driving force is the change in stereochemical activity of the Sb^{3+} lone-pair. The ordering of 2-MIm⁺ counter-cations takes place at lower temperatures and affects the lattice with a step-like contraction in all directions.

Keywords: phase transitions, disorder, modulated structure

MS26-O2

Aperidic structures and luminescent properties in the scheelite family

Vladimir Morozov¹, Artem Abakumov², Joke Hadermann³, Elena Khaikina⁴, Dina Deyneko¹, Bogdan Lazoryak¹, Ivan Leonidov⁵, Dmitry Batuk³, Maria Batuk³

- 1. Chemistry Department, Moscow State University, Moscow, Russia
- Skolkovo Institute of Science and Technology, Moscow, Russia
- 3. Physics Department, University of Antwerp, Antwerp, Belgium
- 4. Baikal Institute of Nature Management, Siberian Branch, Russian Academy of Science, Ulan-Ude, Russia
- Institute of Solid State Chemistry, Ural Branch, Russian Academy of Sciences, Ekaterinburg, Russia

email: morozov111vla@mail.ru

Scheelite (CaWO₄) related compounds $(A', A'')_n[(B', B'')]$ O4], with B', B"=W and/or Mo are promising new materials for red phosphors in pc-WLEDs (phosphor-converted white-light-emitting-diode) and solid-state lasers. Recently a new application field has emerged for these materials due to their ability to visualize temperature gradients with high accuracy and spatial resolution, making them excellent thermographic phosphors. Scheelites can be prepared with a large concentration of vacancies in the A sublattice, giving compositions characterized by a $(A'+A''):(B'O_4+B''O_4)$ ratio different from 1:1. The creation of cation vacancies in the scheelite-type framework and the ordering of A cations and vacancies are a new factor in controlling the scheelite-type structure and properties. Very often the substitution of Ca^{2+} by M^+ and R^{3+} (R^{3+} = rare earth elements) in the scheelite-type structure leads to switching the structure from 3D to (3+n)D (n = 1,2) regime. The creation and ordering of A-cation vacancies and the effect of cation substitutions in the scheelite-type framework are investigated as a factor controlling the scheelite-type structure and luminescent properties of AgxEu(2-x)/3WO4 and Ag_xGd_{(2-x)/3-0.3}Eu_{0.3}WO₄ scheelite-type phases with the variable composition [1]. Transmission electron microscopy also confirmed the (3+1)D incommensurately modulated character of $Ag_x Eu^{3+}_{(2-x)/3}WO_4$ (x = 0.286, 0.2) phases. The luminescent properties of all phases under near-ultraviolet (n-UV) light have been investigated were related to the structural properties of the materials. Ag_xEu_{(2x)/3}WO₄ and Ag_xGd_{(2-x)/3-0.3}Eu_{0.3}WO₄ phosphors emit intense red light dominated by the ${}^{5}D_{0} - {}^{7}F_{2}$ transition at 613 nm, along with other transitions from the 5D0 excited states. Concentration dependence of the 5D0-7F2 emission for AgrEu(2-x)/3WO4 samples differs from the same dependence for the early studied NaxEu3+(2-x)/3MoO4 (0<x<0.5) phases [2, 3]. The intensity of the ${}^{5}D_{0}{}^{-7}F_{2}$ emission is reduced almost 7 times with decreasing x from 0.5 to 0 but it does not change practically in the range from x = 0.286 to x = 0.200. The emission spectra of Gd-containing samples show a completely different trend as compared to only Eu-containing samples. The Eu³⁺ emission under excitation of Eu³⁺(${}^{5}L_{6}$) level (λ_{ex} =395 nm) increases more than 2.5 times with the increasing Gd^{3+} concentration from 0.2 (x = 0.5) to 0.3 (x = 0.2) in the Ag_xGd_{((2-x)/3)-0.3}Eu³⁺_{0.3}WO₄, after which it remains almost constant for higher Gd3+ concentrations. Acknowledgement. This research was supported by Russian Foundation for Basic Research (18-03-00611).

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Keywords: scheelites, aperiodicity, luminesce

MS26-O3

Transitions toward complex electronic states and superperiodic structures in $P_4W_{16}O_{56}$

Elen Duverger-Nédellec1, Alain Pautrat2, Olivier Pérez2

1. XRD department, Charles University, Prague, Czech Republic 2. laboratoire CRISMAT, UMR 6508 CNRS, Caen, France

email: elenduvergernedellec@gmail.com

The MonoPhosphate Tungsten Bronzes (MPTB) family, (PO₂)₄(WO₃)_{2m}, can be described by a regular intergrowth of (PO₄) tetrahedral layers and of slabs constituted by corner-sharing-(WO6) octahedra, with a thickness depending on the m parameter. These low-dimensional oxides are known to exhibit successive transitions toward Charge Density Wave (CDW) states. These transitions are associated to lattice distortions leading to the appearance of incommensurate or commensurate structural modulations [1]. In this family, the electronic anisotropy and the density of carriers of the system can be tuned by modifying the thickness of the WO3 slabs, i.e. changing m. MPTB family is thus a relevant system to analyse the effect of the dimensionality on the CDW electronic instabilities. Temperature-dependant X-Ray Diffraction (XRD) [1] and transport measurements reported in the literature, for different terms of the family, reveal a significant change of behaviour between the terms with a low and high value of m, m < 7 and m > 7 respectively. Classical CDW transitions are reported for the low terms, characterized by a smooth resistivity jump and by the formation of clusters of tungsten in the centre of the WO₂ slabs [2]. For the high terms [3], a structural transition is observed in XRD but the electronic transport studies do not show the usual signature attributed to a CDW. Moreover, the only structural study performed on a high term in the modulated state (m=10) [3] evidences anti-ferroelectric-type (AFE) atomic displacements for the tungsten atoms without reporting of the formation of clusters of tungsten.

We will present both the transport properties and the analysis of the structural modulations for the m=8 term. Three first-order transitions associated with large thermic hysteresis were identified. The analysis of the structural modulations characterizing the different states, via the use of the super-space formalism, reveals the existence of AFE-type displacements and the formation of clusters for the tungsten atoms. These signatures can be assigned to the coexistence of AFE and CDW properties in the material. These two properties are a priori incompatible, but an extensive study of the transport properties versus temperature supports this hypothesis. This result enlightens the very interesting position of $P_4W_{16}O_{56}$ (m =8) in the border area between the low and the high m values in the MPTB family to discuss the competition regime between CDW and ferroelectric instabilities

References:

Keywords: Modulations; Charge-density-wave; Antiferroelectricity

MS26-O4

Protein crystal with ninefold structure modulation and 36 protein molecules in the asymmetric unit

Joanna Śmietańska¹, Joanna Śliwiak², Mariusz Jaskólski², Mirosław Gilski², Zbigniew Dauter³, Radosław Strzałka¹, Janusz Wolny¹

- Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Krakow, Poland
- Center for Biocrystallographic Research, Institute of Bioorganic Chemistry, Polish Academy of Sciences/Department of Crystallography, Faculty of Chemistry, A. Mickiewicz University, Poznan, Polande
- Synchrotron Radiation Research Section, MCL, National Cancer Institute, Argonne National Laboratory, Argonne, United States of America

mail: j.smietanska@autograf.pl

Crystal structure modulation is manifested by the disappearance of short-range translational order with long-range order restored by an atomic modulation function (AMF). In the case of commensurate modulation, when the distortion remains in an integer-multiple relationship with the main lattice, the structure can be described in an expanded supercell or using the superspace concept. On the other hand, incommensurate modulation can be rigorously described only in a higher-dimensional superspace. A physical manifestation of a crystal with structure modulation is the presence of weak satellite reflections around the main Bragg reflections. Although this phenomenon is quite widespread and well-understood in small-molecule crystallography, only a limited number of commensurately modulated crystal structures have been successfully analyzed using the superspace approach [1]. In macromolecular crystallography this phenomenon is practically unheard of. The first successful structure solution and refinement of a modulated protein crystal structure was presented some time ago by us for the Hypericum perforatum PR-10 protein Hyp-1, which in that experiment was crystallized (as a tetartohedral twin) in complex with the fluorescent dye 8-anilino-1-naphthalenesulfonate (ANS) with apparent seven-fold nodulation (and 28 unique protein molecules in the expanded supercell) along the c direction of the C2 space group [2]. In the present project, the same protein was crystallized using different conditions to produce Hyp-1/ANS crystals with nine-fold c-parameter expansion of the same basic C2 unit cell and with 36 protein molecules in the asymmetric part of the expanded supercell. The structure analysis is complicated not only by the length of the c parameter (~400 Å) but also by the tetartohedral twinning of the crystals. Using synchrotron X-ray diffraction data extending to 2.3 Å resolution, the structure was solved by molecular replacement and is being refined, using maximum-likelihood targets, in the expanded supercell under the assumption of commensurate modulation

Keywords: protein, modulation, phytohormone

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MS26-O5

Electronic properties of incommensurately modulated novel and complex materials

Edoardo Martino¹, Alla Arakcheeva¹, Gabriel Autès², Sergiy Katrych¹, Oleg V. Yazyev², Philip J. W. Moll³, Ana Akrap⁴, László Forró¹

- 1. Laboratory of Physics of Complex Matter, École Polytechnique Fédérale de Lausanne EPFL, Lausanne, Switzerland
- National Centre for Computational Design and Discovery of Novel Materials MARVEL, École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland
- Max-Planck-Institute for Chemical Physics of Solids, Dresden, Germany
- Light Fermion Spectroscopy group, University of Fribourg, Fribourg, Switzerland

email: edoardo.martino@epfl.ch

Potential periodicity in crystalline materials define their band structure and ultimately their electronic properties. An open question is how electronic properties are altered when two incommensurate potentials cohexists. In our research we aim at understanding the structure-properties relation for metals with incommensurately modulated structure.

In our recent work we investigated the new compound $Sr_2Pt_{s,x}As$, synthesised at high pressure and high temperature. The Pt vacancies (x=0.215) located only on one specific site, are long range ordered and incommensurately modulated. We attribute to the structural modulation the saturation of electrical resistivity, with a peculiar temperature variation of less than 5% from room temperature to 4.2 K. The mechanism of resistivity saturation was described by Belitz and Schirmacher, [1] as quantum interference of conduction electrons by a high density of scattering centers, and identified as universal behaviour in "disordered" metals by Mooij [2].

Our goal is to bridge the structural studies and properties investigation, to clarify the commonly undefined term of "disorder" and understand the role of incommensurated structural modulation.

I will also outline our following research on layered transition metal dichalcogenides, a group of well studied materials, where local lattice distortion due to formation of charge density wave results in modulated structures.

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Keywords: structure-properties, incommensurately modulated structure, Mooij correlation

MS27 Quasicrystals: theory and experiment

Chairs: Prof. Marc de Boissieu, Prof. Janusz Wolny

MS27-01

Clusters in the Al13TM4 quasicrystalline approximants : role on the surface structures and properties

Émilie Gaudry1

1. Univ. Lorraine CNRS IJL, Nancy, France)

email: Emilie.Gaudry@univ-lorraine.fr

A wide range of intermetallic crystal structures are based on polyhedral entities, often called "clusters", as first introduced by F.A. Cotton in the early 1960's to describe compounds containing metal-metal bonds. This approach is also largely used to describe more complex intermetallic phases, like quasicrystals and their approximants. Termed four-layer decagonal approximants, the structures of the $Al_{13}TM_4$ compounds (TM = transition metal, like Co, Fe, Ru for the experimentally grown compounds) have been initially understood as a periodic stacking of pseudo-10-fold symmetric atomic layers, but are also described a three-dimensional stacking of 26-atom clusters.

While the bulk atomic arrangements of the $Al_{13}TM_4$ compounds are very similar, the structures of their pseudo-10fold surfaces differ. The cluster substructure is preserved up to the $Al_{13}Fe_4(010)$ surface, but $Al_{13}Co_4(100)$ presents an Alrich dense termination. The situation is even more complex for $Al_{13}Ru_4(010)$, since a surface reconstruction is observed experimentally [1]. Such structural differences lead to contrasted surface properties, for example in catalysis [2].

A systematic determination of the bulk electronic structure and chemical bonding network in the Al13TM4 series, including hypothetical compounds (TM= Mn, Fe, Co, Ni, Ru, Rh, Os, Ir) is an essential step in the scope of understanding the stabilities of the structures for TM = Fe, Co, Ru, as well as the surface structures and properties. This is achieved here with a theoretical approach based on the Density Functional Theory (plane-wave implementation). The projected Crystal Orbital Hamilton Population (pCOHP) has been used to analyze the chemical bonding network [3]. This method re-extract Hamilton-weighted populations from plane-wave electronic structure calculations to develop a tool analogous to the crystal orbital Hamilton population method. The bonding strengths result from the pCOHP integration to the Fermi level. While variations are noticeable within the Al13TM4 series, as will be discussed in the talk, the general picture leads to a decrease of the bonding strength with the bonding distance.

These insights into the chemical bonding network of the $AI_{13}TM_4$ compounds are very useful for the understanding of their diverse surface structures and properties. It also enable the discussion of chemical-composition / crystal-structure / (surface) properties relationships.



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Keywords: Al13TM4, chemical bond, cluster

MS27-O2

Anisotropic quantum critical point in the Ce₃Al intermetallic compound

Janez Dolinsek1

1. Solid State Physics Department, Jozef Stefan Institute, Ljubljana, Slovenia

email: jani.dolinsek@ijs.si

A quantum critical point (QCP) is a point in the phase diagram of a material where a continuous phase transition takes place at absolute zero temperature [1,2]. Quantum phase transitions at T = 0 are driven by zero-point quantum fluctuations associated with Heisenberg's uncertainty principle, in contrast to conventional (thermodynamic) phase transitions that occur at a nonzero temperature and are driven by thermal fluctuations. A QCP is typically achieved by a continuous suppression of a thermodynamic phase transition to zero temperature by the application of a magnetic field, pressure or through doping. Quantum phase transitions arise in guantum many-body systems as a result of competing interactions that foster different ground states. An example are the RKKY exchange interaction and the Zeeman interaction of spins with the external magnetic field, where a continuous increase of the field can induce a quantum phase transition from a magnetically ordered state to a paramagnetic state via tuning the degree of quantum tunneling between the "up" and "down" spin-polarized states.

Based on the magnetic susceptibility, magnetoresistance and specific heat measurements, we determined the anisotropic, magnetic field driven QCP in the magnetically anisotropic Ce₃Al compound that exhibits both antiferromagnetic (AFM) ordering and heavy fermion behavior. The QCP in the Ce₃Al results from competition of the RKKY exchange and the Zeeman interactions on the Ce-Al chains, where the Ce moments order AFM at $T_{\rm N} = 2.6$ K, whereas the moments on the Ce-Ce chains are Kondo-compensated and do not participate in the QCP formation. External magnetic field drives the AFM transition continuously toward zero temperature for the field applied in the monoclinic (a,b)easy plane, reaching the QCP at the critical field value $B_c =$ 4.2 T, where a transition from the AFM to a spin-flop state takes place. For the field applied along the perpendicular cdirection, the QCP does not occur. The anisotropy of the OCP with regard to the direction of the magnetic field in the crystal lattice is a consequence of large, crystal-fieldsinduced magnetic anisotropy, which locks the magnetic moments into the easy plane and cannot be overcome by the two competing interactions. The QCP in systems with large magnetic anisotropy is generally anisotropic and the experiments to observe this anisotropy should necessarily be performed on monocrystalline samples.

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Keywords: quantum critical point, quasicrystals and approximants

MS27-O3

Application of the Generalized Penrose Tiling to the structure refinement of AlCuRh decagonal quasicrystal

Radosław Strzałka¹, Ireneusz Bugański¹, Maciej Chodyń¹, Janusz Wolny¹

1. Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Krakow, Poland

email: strzalka@fis.agh.edu.pl

In our presentation we will show the refinement results of the AlCuRh decagonal quasicrystals with application of the Generalized Penrose tiling (GPT) as a quasilattice. The applicability of the GPT to structural modeling of decagonal systems was widely studied by Chodyn et al. [1], whereas the atomic structure of AlCuRh was previously investigated by Kuczera et al. [2]. In both papers [1,2], as well as in our studies, the statistical method based on the average unit cell concept was used [3]. The GPT-based model consists of additional fifth atomic surface, which size is dependent on the shift along z-axis in multidimensional hyperspace. Alongside, all other pentagonal atomic surfaces become non-uniform decagons. The subdivision of the atomic surfaces (as well as average unit cells) into regions corresponding to a particular structural unit (thick of thin rhombus) at a given orientation gives now hexagons instead of triangles. All these features of the GPT introduce completely new local arrangements of thick and thin rhombi, not observed for the regular Penrose tiling. A quasilattice obtained from the GPT gives more freedom in the refinement, which is promising in achieving better refinement results of real systems. The GPT model was already applied to model decagonal quasicrystals and simple decorations with atoms. Now we show the refinement results for the decagonal AlCuRh. This is the first application of the GPT to real decagonal system in literature. The starting decoration was derived from the electron density maps, obtained from the diffraction data collected previously by Kuczera. New families of unit tiles' arrangement (created by the additional fifth atomic surface) were decorated in the same manner as all others. The refinement was converged with R-factor of 6.52%, which is a significant improvement comparing to 7.9% reported in the original paper [2]. The comparison of the two models will be presented and details of the new results will be discussed.

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Keywords: decagonal AlCuRh, generalized Penrose tiling, statistical method

MS27-O4

Is PdBi the little brother of AuIn?

Laura Folkers1, Sven Lidin1

1. Department of Chemistry, Lund University, Lund, Sweden

email: laura.folkers@chem.lu.se

Recently the structure of the AuIn 1:1 phase was elucidated [1], showing its structural changes with temperature. The first indicators for uncommon behaviour in AuIn was the fact that the structure was unknown, despite the simple stoichiometry. A second peculiarity is the difficulty of growing a single crystal of this material. However the main indicator is the Differential Scanning Calorimetry (DSC) data shown in the top panel of Figure 1. At a temperature of 443°C the DSC curve signals the melt of a super structure, while the full structure only melts at 515°C. Only with this information growth of a suitable single crystal was possible, and this could be used to obtain the here presented diffraction data. This data showed that AuIn, believed to be of the thallium iodide type [2], actually only shows this structure above the temperature of 443°C and at lower temperatures undergoes first a Peierls type distortion before it becomes incommensurate [1].

PdBi turns out to be a similar case, where a 1:1 intermetallic, which normally display simple structures turns out to be quite complex. The atomic positions of the reported structure of the HT phase of this compound correspond to the TII type structure [3].

Even more importantly, the DSC measurement shows precisely the same pattern as for AuIn (see Fig.1, bottom). A first melting event occurs at 583°C, a second one at 635°C and a solidification peak can be seen at 569°C.

A recent synchrotron study of PdBi shows that it indeed follows the expected behaviour. Between room temperature and 300°C, preliminary data treatment has shown that the structure transforms from a commensurate 2x2x2 super structure, via an incommensurate structure, to a disordered structure. This is indicated by satellite positons slightly changing place and eventually satellites turning into diffuse scattering.

The precise behaviour of PdBi with respect to temperature will be discussed in detail in the presentation.



DSC measurement of AuIn sample





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Teoreticheskoi Fiziki', 5, 1064 - 1072.

Keywords: Aperiodics, Intermetallics, Synchrotron Data

MS27-O5

Adventures in modulation: derivatives of barluenga's reagent

Amber L. Thompson¹, Lewis C. F. Morgan¹, Yejin Kim¹, Emma J. McKinley¹, Jack N. Blandy², Claire A. Murray³, Kirsten E. Christensen¹

- 1. Chemical Crystallography, Department of Chemistry, University of Oxford, Oxford, United Kingdom
- 2. Department of Chemistry, University of Oxford., Oxford, United Kingdom
- Diamond Light Source Ltd, Harwell Science and Innovation Campus., Didcot, Oxfordshire., United Kingdom

email: amber.thompson@chem.ox.ac.uk

Single-crystal X-ray diffraction is a powerful technique: as the technique has developed data collections have been getting faster and faster, and structure determination is becoming more routine. There are an increasing number of non-expert users collecting data, solving and refining structures before publishing their own results. However, with the advent of higher intensity laboratory X-ray sources, easier access to synchrotron radiation and more sensitive detectors, more and more molecular structures are showing alien features beyond the realms of conventional crystallography [1].

Though the concept of modulated structures is now fairly well established in solid state chemistry, the abundance of reported modulated molecular materials is less than might be expected. There are a number of probable reasons for this, including the fact that the synthetic chemist is primarily interested in connectivity and proof of what they have made, so they are not curious about additional peaks seen in a diffraction pattern. When tweaking the synthesis and/or changing crystallisation conditions makes the curious extra features disappear, this is typically the chosen route and the original structure is casually swept under the carpet.

When a concerted effort is made to study the appearance of additional satellite reflection and relating it to changes within the structure, valuable extra information can be gained concerning molecular packing and the crystalline state. One such example is found in Barluenga's reagent, IPy₂BF₄ (Py = pyridine) [2], which has been shown to exhibit a transient modulated phase on cooling (see image). Systematic studies on derivatives of Barluenga's reagent have been carried out in which the pyridine is replaced with 2,4,6-trimethyl pyridine (collidine, Coll), iodine with bromine and the BF₄ anion is replaced with other small anions including ClO₄ and PF_6 [3]. Through these changes to the chemistry we can begin to understand how the crystal structure and the diffraction pattern are related and why satellite peaks may appear, with the aim of improving our understanding of the mechanism governing the appearance of modulation in molecular materials.



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Keywords: Modulation, Barluenga's Reagent, Variable Temperature

MS28 Magnetic order: methods and properties

Chairs: Dr. Francoise Damay, Prof. José L. García-Muñoz

MS28-O1

On the symmetry of incommensurate magnetic structures

J. Manuel Perez-Mato¹, Luis Elcoro¹, Gotzon Madariaga¹, Mois I. Aroyo¹

 Dept. Fisica de la Materia Condensada, Facultad de Ciencia y Tecnologia, Universidad del Pais Vasco, UPV/EHU, Bilbao, Spain

email: jm.perezmato@gmail.com

The concept of symmetry in materials science trascends the role of being just a mere mathematical or geometrical property. In general, the symmetry of a crystal, within a certain thermodynamical phase, is an intrinsic physical property of the phase (phase transitions can occur without a symmetry change, but a symmetry change cannot happen without a phase transition!). In this sense, the symmetry of a crystal can be considered a thermodynamical property, which will be preserved by any possible physical atomistic mechanisms that may be active in the system as long as no phase transition occurs.

The symmetry of aperiodic crystals (structures that are ordered, but lack periodicity), is given by the so called superspace symmetry groups. As required of any well-defined generalized symmetry, these symmetry groups satisfy the above mentioned physical condition of being an intrinsic property that is necessarily preserved within a thermodynamical phase. This generalized symmetry formalism was introduced in the seventies to describe the symmetry properties of incommensurately modulated crystals, and in the next decade was further extended and applied to quasicrystals. Nowadays the formalism is fully established, and since decades superspace groups are used in a routinary and systematic way to characterize incommensurate and quasicrystalline structures.

Although the superspace formalism is easily extensible to incommensurate magnetic structures, its application to magnetic systems has remained scarce until recently. Only in the last years the development of specially adapted computer tools, and in particular, the extension of the JANA refinement program to magnetic structures has changed the situation. Using these freely available tools, superspace symmetry formalism can now be applied and this allows an efficient and rigorous description of incommensurate magnetic structures making full use of their symmetry. An additional step in this direction has been the development in the Bilbao Crystallographic Server of a small database of such structures (www.cryst.ehu.es/magndata), where the magnetic superspace group of each structure have been identified and their efficient decription using this symmetry group is shown in detail.

In this talk I will review the concepts of magnetic superspace symmetry and its application. The relation with the traditional representation method will be discussed, stressing their complementarity. Some examples retrieved from the mentioned database will help to show how representation analysis and superspace symmetry can be combined to achieve an optimal enumeration of possible physically-distinct incommensurate magnetic orderings and to obtain a detailed unambiguous rigorous characterization of magnetically modulated structures.

Keywords: incommensurate magnetic structures, supespace symmetry, magnetic symmetry

MS28-O2

Complex magnetic structure of the swedenborgite CaBa(Co₃Fe)O₇ derived by unpolarized neutron diffraction and spherical neutron polarimetry

Navid Qureshi¹, María Teresa Fernández-Díaz¹, Laurent Chapon², Anatoliy Senyshyn³, Werner Schweika⁴, Martin Valldor⁵

- 1. Institut Laue-Langevin, Grenoble, France
- 2. Diamond Light Source, Didcot, United Kingdom
- Forschungs-Neutronenquelle Heinz Maier Leibnitz (FRM-II), Garching, Germany
- Institut f
 ür Festk
 örperforschung, Forschungszentrum J
 ülich, J
 ülich, Germany
- 5. Leibniz Institute for Solid State and Materials Research, Dresden, Germany

email: qureshi@ill.fr

The magnetic swedenborgites, i.e. structural homologues to the hexagonal mineral SbNaBe₄O₇ (Refs. [1,2]), contain kagome layers with several different, similarly strong, competing spin interactions, which lead to a wide variety of ground states including chiral spin liquids), spin-glasses and long-range antiferromagnetic order. The slight structural distortions away from the hexagonal symmetry release the geometric frustration and the nature of the distortion determines the ground state. As the spins are Heisenberg-like, a Néel order is not expected unless a significant magnetic coupling between the kagome layers is at hand, which is mediated by triangular layers in-between. Here we present an extensive study on the orthorhombic compound CaBa(Co3Fe)O7 combining powder and single-crystal neutron diffraction as well as spherical neutron polarimetry (SNP). A detailed analysis of the possible irreducible representations and the magnetic structure factors in combination with the observed polarization matrices of special reflections gave clear indications concerning the magnetic symmetry. The complex situation with the presence of three structural twins and four magnetic domains (two orientational and two chiral domains) was tackled with the development of a unique software, Mag2Pol [3], which permits the refinement of a magnetic structure model including domain populations to integrated intensity and SNP data simultaneously. We could therefore derive an interesting magnetic structure of magnetic superspace symmetry P2'_1, which differs from any other member of the swedenborgite family, but which can be mapped onto the classical sqrt(3) x sqrt(3) structure of a kagome lattice. The resulting spin structure indicates an important interplay between the kagome and the triangular layers of the crystal structure.

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Keywords: magnetic structure, neutron diffraction, spherical neutron polarimetry

MS28-O3

New dedicated neutron scattering instrument for complex magnetic structures POLI

Hao Deng1

 Institute of Crystallography, RWTH Aachen University and Jülich Centre for Neutron Science (JCNS) at Heinz Maier-Leibnitz Zentrum (MLZ), 85748 Garching, Germany, Garching bei München, Germany

email: darkhunterak@gmail.com

As one of the most powerful methods for investigating nuclear and magnetic structures, neutron diffraction (especially polarized neutron diffraction) plays a key role in better understanding complex magnetic and domain configuration in multiferroics, heavy fermion superconductors, frustrated systems and other complex magnetic materials. Polarized single-crystal diffractometer POLI at MLZ^[1] employs non-polarized double-focusing monochromators in combination with high-efficiency ³He cell polarizers, which lead to a gain in both flux and resolution in comparison with other short-wavelength polarized neutron diffractometers using Heusler-alloy monochromators. With flexible instrument setups, namely: (1) classical single crystal neutron diffraction in extreme environments like high magnetic fields, very low/high temperatures, high voltage, pressure cells etc. and their combinations; (2) polarize neutron diffraction (flipping-ratio measurements) using high magnetic field^[2] and (3) zero-field spherical neutron polarimetry (SNP) using the third generation Cryopad^[3]. and rather high flux of hot polarized neutron, POLI raises to a powerful tool in complex magnetic structure research. In this report, we will show the strength of instrument in study magnetic structures. Several examples of applications in resolving different challenging aspects in crystal, magnetic and domain structure of complex magnetic material will be presented. Examples of (1) basic magnetic structure refinement, (2) magnetic structure studies under very low temperature and high pressure, (3) distinguish magnetic spin density wave, helicoidal or cycloidal chiral structures, (4) separate incommensurate structures with very long period, (5) magnetic domain study with depolarization analysis using SNP setup. Our versatile instrument gives a unique access to understanding complicated magnetic structures and offers a good starting point for further exploring dynamics in novel magnetic physics.

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Keywords: Polarized neutron diffraction, complex magnetic structures

MS28-O4

Revisiting the magnetic structure of La_{1/3}Sr_{2/3}FeO₃ by neutron powder diffraction

Fei Li¹, Vladimir Pomjakushin², Romain Sibille², Ruchika Yadav³, Lukas Keller², Marisa Medarde¹, Kazimierz Conder¹, Ekaterina Pomjakushina¹

- 1. Laboratory for Multiscale Materials Experiments, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland
- Laboratory for Neutron Scattering and Imaging, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland
- Laboratory for Scientific Developments and Novel Materials, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland

email: fei.li@psi.ch

 $La_{1/3}Sr_{2/3}FeO_3$ is reported to show a $2Fe^{4+} \rightarrow Fe^{3+} + Fe^{5+}$ charge disproportionation (CD) accompanied by Fe3+/Fe5+ charge ordering (CO) and a metal-insulator (MI) transition at 200 K [1]. The MI transition was ascribed to CD and CO. Based on the CO, the magnetic structure was reported to be P-3m1 or P1 from the neutron diffraction studies performed at 50 K and 15 K, respectively [2]. The former seems not to be a correct solution since the presence of rotoinversion -3 is incompatible with the claimed collinear magnetic structure, with the collinear moments in the ab-plane in R-3c metric; and the latter might be a correct solution, but without any symmetry restrictions in space group P1. In this study, the magnetic ordering this compound has been revisited by neutron powder diffraction down to 2 K [3]. From full symmetry analysis, a chiral helical model and a collinear model are proposed. The neutron diffraction pattern is equally well fitted by either model.

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Keywords: magnetic structure, neutron powder diffraction

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MS28-O5

Magnetic structure determination of EuPtIn₄ through resonant X-ray magnetic scattering

Pablo J. Bereciartua¹, Jose R. L. Mardegan¹, Sonia Francoual¹, P. Rosa², Juan Rodríguez-Carvajal³, Larissa S. I. Veiga¹, Frédéric-Emmanuel Picca⁴, M. Saleta², Joerg Strempfer¹

- 1. PETRA III, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany
- Instituto de Física "Gleb Wataghin", Universidade Estadual de Campinas, Campinas, Brazil
- 3. Institut Laue-Langevin (ILL), Grenoble, France
- 4, SOLEIL synchrotron, Saint-Aubin, France

email: pablo.bereciartua@desy.de

Zintl phases are ionic intermetallic compounds characterized by a polyanionic network with covalent bonds. These compounds are studied because of their structural variability and their electronic and physical properties [1,2]. An interesting case is the compound EuPtIn4, which presents a phase transition from a paramagnetic to an antiferromagnetic structure below a Néel temperature of 13 K and for which a spin-flop transition was observed under a high magnetic field applied along the ac-plane at low temperature. Due to the strong neutron absorption of Eu, the resonant X-ray magnetic scattering (RXMS) technique was employed to investigate the magnetic structure in EuPtIn4, taking advantage of the significant enhancement of the magnetic signal obtained at the L2 edge of Eu. The RXMS experiments were performed at beamline P09 of PETRA III. employing different experimental possibilities, including a double phase retarder for full polarization analysis and a vertical 14 T cryomagnet [3]. The measurements confirm the phase transition at the mentioned Néel temperature and reveal an incommensurate antiferromagnetic structure with a propagation vector $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, \gamma)$, where γ is the incommensurate component with a value of 0.4258. The intensities of a set of reflections with indices $(\frac{1}{2}, n + \frac{1}{2}, \gamma)$ have been measured in the $\sigma\pi$ ' channel (with *n* being an integer between 6 and 14) to infer the magnetic structure in the ground state while full linear polarization analysis was used to study the changes under high magnetic fields. Hereby, we will report on the magnetic structure of EuPtIn4 as solved using the equations for RXMS and the density matrix formalism and on its corresponding magnetic superspace group.

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Keywords: magnetic structure, resonant X-ray scattering, superspace formalism

MS29 Mathematical crystallography: special aspects of symmetry and other topics

Chairs: Prof. Berthold Stöger, Prof. Bernd Souvignier

MS29-01

Z-modules in crystallography: structures and defects

Marianne Quiquandon¹, Abdullah Sirindil¹, Raphaël Kobold², Frédéric Mompiou³, Sylvie Lartigue-Korinek³, Loïc Perriere³, Gilles Patriarche⁴, Denis Gratias¹

- 1. IRCP Chimie ParisTech-CNRS, Paris, France
- 2. Institute of Material Physics in Space, German Aerospace Center (DLR) Cologne, Germany
- 3. CEMES-CNRS, Toulouse, France
- 4. C2N-CNRS, Marcoussis, France

email: marianne.quiquandon@chimie-paristech.fr

Z-modules¹ are natural extensions of lattices. They have been introduced in crystallography by A. Janner and T. Janssen [1] *in reciprocal space* as the convenient tool to index the diffraction diagrams of incommensurate phases using a set of N integers (N > d, d being the dimension of the physical space). This generated the idea of extending crystallography to N-dimensional spaces, defining thus super-periodic crystals (incommensurate phases, composite crystals and quasicrystals).

Our present goal is to discuss the consequences of the presence of Z-modules of rank N in direct space in the crystallographic description of certain structures, revealing thus hidden symmetries when embedded in a N-dimensional superspace: what kind of new defects could possibly be generated when the atoms of the crystal are located on a long range ordered subset of the nodes of a Z-module? [2,3]

After recalling the basic definitions and properties of Z-modules, we exemplify the embedding process from d- to N-dimensional spaces, using the specific case of the NiZr orthorhombic *Cmcm* structure that is fully defined on a single Z-module generated by the vertices of the regular pentagon. We will then explain the symmetry breaking in the process of backwards projection from N- to d-dimensional spaces that generates the defects leaving the module invariant but not the crystal. In NiZr, there are essentially two such basic defects: a quinary twin and a translation boundary (plus its corresponding dislocation).

Observations by HREM and HAADF electron microscopy show the perfect agreement at the atomic level between theoretical models and experiments. This justifies the physical pertinence of introducing Z-modules in the crystallography of those kind of alloys that have local hidden non crystallographic symmetries.

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1 A Z-module of rank N in Rd with N>d is the set S of points of Rd that are linear combinations with integer coefficients of N vectors arithmetically independent:

- a Z-module of rank N in Rd is the (irrational) projection of a lattice ZN in RN;

- a Z-module of rank N in Rd forms an enumerable dense set of points in Rd or in a non-empty subspace of Rd;

- if d = N the Z-module is trivially a lattice ZN.

Keywords: Z-modules, twins, dislocations

MS29-O2

The theory of twisted X-rays and their diffraction patterns

Dominik Jüstel¹, Gero Friesecke², Richard James³

- 1. Institute for Biological and Medical Imaging, Helmholtz Center Munich, Munich, Germany
- 2. Department of Mathematics, Technical University of Munich, Munich, Germany
- 3. Department of Aerospace Engineering and Mechanics, University of Minnesota, Minneapolis, United States of America

email: dominik.juestel@helmholtz-muenchen.de

Most molecular structures that are known today have been found by X-ray crystallography. However, a main drawback of the method is the need to crystallize the structures under consideration. As proteins often do not form crystals, but aggregate in other highly symmetric assemblies, like rods or sheets, we proposed to design electromagnetic radiation that reflects the symmetry of the structures in the same way as plane waves do for crystals [1,2].

In the special case of heliclal structures, like carbon nanotubes or helical viruses, this approach yields a class of radiations that we call twisted X-rays [1,2], and that are closely related to X-ray beams carrying orbital angular momentum [3].

In this talk, the theory of twisted X-rays and their diffraction patterns will be presented. Furthermore, it will be shown that structure analysis using twisted X-ray diffraction has the potential to solve molecular structures that are recently unaccessible.

Keywords: twisted X-rays, orbital angular momentum


Bilbao Crystallographic Server – new databases and computer tools for the study of layer and multilayer materials

Gemma de la Flor Martin¹, Danel Orobengoa¹, Yuri E. Kitaev², Robert Evarestov³, Luis Elcoro¹, Gotzon Madariaga¹, Mois I. Aroyo¹

- 1. Departamento Física de la Materia Condensada, Universidad del País Vasco UPV/EHU, Bilbao, Spain
- Laboratory of Quantum-size Hererostructures, Ioffe Institute, Saint Petersburg, Russia
- Institute of Chemistry, Saint Petersburg State University, Saint Petersburg, Russia

email: gemma.delaflor@ehu.es

The Bilbao Crystallographic Server (www.cryst.ehu.es) [1-2] is a free web site that grants access to specialized databases and tools for the resolution of different types of crystallographic, structural chemistry and solid-state physics problems. The server is in constant improvement and development, offering free of charge tools to study an increasingly number of crystallographic systems. Recently, new tools dedicated to the study of materials with layer and multilayer symmetry have been developed due to the arising interest in these type of materials. The purpose of this contribution is to report on the current state of the server emphasizing on the recently developed computer tools for the study of materials with layer group symmetry. The utility of the available applications will be demonstrated by illustrative examples.

The section Subperiodic groups: Layer, Rod and Frieze Groups gives access to the layer groups databases containing the basic crystallographic information, and the Brillouin-zone and k-vectors tables that form the background and a classification of the irreducible representations (irreps) of the 80 layer groups. The programs GENPOS, WPOS, MAXSUB and KVEC provide access to the general positions, Wyckoff positions, maximal subgroups and Brillouin-zone databases, respectively. More complex tools such as the program SECTIONS that identifies the layer symmetry of space-group sections are also accessible in this section. This program calculates the full set of possible layer symmetries of periodic sections defined by their common normal vector and located within the unit cell for a given space group. The last tool to join this section is the program LSITESYM which is based on the so-called site-symmetry approach [3] that established symmetry relations between the localized state (local atomic displacements) and crystal extended states (phonon, electrons, etc.) over the entire Brillouin zone. The method is based on the procedure of induction of representations of the layer group of the crystal from the irreps of the site-symmetry groups of constituent units (atoms, clusters and layers) according to which the local excitations are transformed. For a given layer group, k-vector and a selected representative of a Wyckoff position, the program LSITESYM returns the symmetry operations of the site symmetry group, its irreps and the irreps of the crystal layer group according to which transform the compatible extended states.

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Keywords: subperiodic groups, bilbao crystallographic server, symmetry

MS29-O4

Symmetry breaking via hybrid improper mechanisms in molecular perovskites

Hanna Boström1, Mark Senn2, Andrew Goodwin1

University of Oxford, Oxford, United Kingdom
 University of Warwick, Warwick, United Kingdom

email: hanna.bostrom@chem.ox.ac.uk

Ferroelectricity, *i.e.* the presence of a switchable electronic polarisation, is an attractive property with commercial applications; yet the realisation of ferroelectric materials can be challenging due to the requirement for a polar space group. In the well-studied perovskite oxides, polar space groups mainly arise from the off-centring of the B-site metal ion—as in BaTiO₃—or the presence of a stereochemically active lone pair—as in BiFeO₃. However, these mechanisms impose severe restrictions on the nature of the cations and hence limit the scope for the discovery of new ferroelectrics.

In light of this, hybrid improper ferroelectricity (HIF) is an attractive phenomenon as it arises from structural, rather than compositional, factors.1 It relies on the coupling of two non-polar distortion modes, which collectively lift the global inversion symmetry and induce a polar secondary order parameter. Hence, group theory is a valuable tool for enumerating the possible coupling schemes of primary order parameters which may reasonably be expected to couple to a non-centrosymmetric mode and hence break global inversion symmetry. One of the canonical HIF materials is the Ruddlesden-Popper oxide Ca3Mn2O7, which may be described as a layered perovskite, and its superimposed primary order parameters are the two tilt modes transforming as X2+and X3-1. However, in simple three-dimensional perovskites, hybrid improper couplings are not feasible as all tilt modes preserve the inversion centre at the B-site in the ABO₃structure. As a result, ferroelectric bulk perovskites without layered order are rare. However, in recent years, several coordination polymers with the perovskite topology have been reported and they exhibit distortions with periodicities forbidden in inorganic perovskites, e.g. unconventional tilting and columnar shifts.2

Here, we present a group-theoretical study of hybrid improper ferroelectricity in these molecular perovskites. We identify primary order parameters that may couple to a non-centrosymmetric, and generally polar, distortion mode. Due to the larger library of symmetry-breaking distortions, molecular perovskites can adopt acentric structures even in the absence of layered order and have a higher propensity for hybrid improper ferroelectricity relative to their inorganic counterparts. Not only do our results rationalise a number of acentric compounds found in literature; it may also be used as a tool for the prediction of new, as-yet unrealised polar materials.³

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 submitted, arXiv:1712.01306.

Keywords: hybrid improper ferroelectricity, group theory, coordination polymers.

MS29-O5

Crystallographic explorations into uniform distribution theory

Wolfgang Hornfeck1

1. Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic

email: hornfeck@fzu.cz

The crystallographic methods applied in structural chemistry for the description of crystal structures focus on a few recurring principles, among them the closest packing of spheres and space group symmetry. While the former concept is locally quantitative, e.g. by giving each atom a coordination number, it rarely offers a similar quantitative global description. The latter concept, however, while being an inherently global descriptor, is purely qualitative. For instance, every so often it happens that crystal structures, e.g. ones related by a phase transition, are very distinct in their symmetry, while being very similar in their local arrangement of atoms at the same time. In other cases, on the contrary, a point can be made for the distinction of structures, although they belong to the same family of structures sharing the same space group symmetry. Moreover, cases exist, in which the arrangement of atoms can be described in ways extending their formal space group symmetry, e.g. by algebraic relations. Thus, it appears to us, that one should search for other concepts, capable of capturing some of these 'hidden symmetries', and in a preferably quantitative and global manner. This is especially true for the description of extended solids, since qualitative and quantitative structural descriptors are well-known for molecules, for which they are successfully used in establishing structure-activity relationships. Here we report about our explorations into the realm of uniform distribution theory, in particular geometric discrepancy theory [1], applying measures for the (ir)regularity of distribution of atoms in space in an crystal chemical context. We highlight examples for the application of the star discrepancy measure in distinguishing variations of a crystal structure belonging to the same general family of structures [2], as well as relations of the diaphony measure to the description of X-ray diffraction by means of the structure factor equation [3].

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Keywords: uniform distribution, star discrepancy, diaphony

MS30 Halogen and chalcogen bonding in the solid state

Chairs: Dr. Guillermo Minguez, Prof. Giuseppe Resnati

MS30-O1

Chalcogen bonding in synthesis and design of arylhydrazone dyes

Kamran Mahmudov¹, Atash Gurbanov¹, Armando Pombeiro¹

1. Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Lisbon, Portugal

email: kamran_chem@yahoo.com

Inter- and intramolecular noncovalent interactions (hydrogen, aerogen, halogen, chalcogen, pnicogen, tetrel and icosagen bonds, as well as cation- π , anion- π , π - π stacking, n- π^* , agostic, anagostic, lipophilic, etc. interactions) play a crucial role in the synthesis, crystal engineering, structural organization of biochemical systems, molecular recognition, drug delivery and design, decoration of materials, electrochemical immobilization and catalysis.1 Among these weak forces recently explored, chalcogen bonding has received a particular attention in view of its directionality, hydrophobicity, tunability, donor atom size and multiplicity.2 These properties have successfully been utilized in catalysis, construction of co-crystals or ions having complementary acceptor and donor sites. Similarly to the hydrogen bonds,3 the chalcogen bonds are classified into several fundamental types: negative charged assisted (Ch···D-), positive charged assisted (Ch+····D), conventional (or "neutral") (Ch···D) and resonance assisted chalcogen (RAChB) bonds.² In comparison to other types of chalcogen bonding the RAChB was only theoretically highlighted, concerning a kind of intramolecular Ch-bonding strengthened by a conjugated *p*-system in multi-membered ring(s). The lecture will demonstrate the role of RAChB in the synthesis and design of arylhydrazones of sulfamethizole.

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Keywords: Chalcogen bonding, Noncovalent interactions, Hydrazone dyes

MS30-O2

Halogen-bonding mediated reactions

Marta Elena Gonzalez Mosquera¹, Pilar Gomez-Sal¹, Silvia Dortez¹, Carlos Gaiteiro¹, Miguel Palenzuela¹

1. stry, Alcala de Henares, Spain

email: martaeg.mosquera@uah.es

Along this century, the importance of halogen bonding has been increasingly acknowledged specially in molecular recognition processes, as structural directing tool and in some physical properties.[1] However, an area whose influence has been less studied is its role in reactivity, even though halogen bonding interactions can be found at the starting point of some chemical processes.[2]

In our group we are interested in the preparation of halogen bonding supramolecular organometallic networks, containing either main group or transition metal complexes. In these studies, we have observed that the formation of this XB interaction is the first step to the substitution reactions of halide ligands in isocyanide transition metal complexes of the type [Ru(X)2(CNR)4] when reacted with Br2 or I2.[3] The reaction takes place independently of which one is the halogen used and the halide ligand, although the reaction rate varies depending on the nature of the halogens. As well the electronic density on the metal influences the reaction rate. The extension of these studies to other co-ligands such as arene groups shown that the process also takes place and new species can be generated, as shown in the figure. The study of these systems has led to a whole range of XB-based networks were Cl...Br, Cl...I, Br...Br, I...I and I...Br are present which has allowed us to perform a comparison of the XB parameters for the different networks isolated. We have also extended this work to organic molecules, in this case a halide abstraction by halogen bonding has been detected in a process that led to the formation of new C-S bonds. The influence of halogen bonding in the reactivity, either in metallic complexes or in organic molecules, gives a dynamic picture for this interaction and expands even further its applications.



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Keywords: XB networks, ruthenium complexes, substitution reactions

MS30-O3

Thiazoliums and selenazoliums as Chalcogen Bond donors in crystals

Patrick Scilabra¹, Konstantis F. Konidaris¹, Giancarlo Terraneo¹, Giuseppe Resnati¹

 Laboratory of Nanostructured Fluorinated Materials (NFMLab), Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Via L. Mancinelli 7, 20131, Milano, Italy

email: patrick.scilabra@polimi.it

In-depth understanding of weak bonds, commonly named interactions, is essential in designing and tailoring of a wide variety of properties in supramolecular chemistry, crystal engineering, materials science, and biology. A detailed comprehension is available for some noncovalent interactions, and this is the case, for instance, for the well-known Hydrogen (HB) and Halogen bonds (XB). A substantially more limited set of information is available for some other weak bonds. The ongoing IUPAC project n° 2016-001-2-300 (https://iupac.org/projects/project-details/?project nr=2016-001-2-300) aims to register the emerging consensus on proposals suggesting to use terms Chalcogen, Pnictogen, and Tetrel bonds exclusively for interactions wherein Groups 14-16 elements are the electrophile sites [1]. The purpose of this research is to partially fill this dearth of information by exploring the potential of Chalcogen Bond (CB) which is the attractive interaction wherein an element of Group 16 is the electrophilic site [2]. While there is a plethora of papers examining CB from the theoretic point of view, the experimental studies on this weak bond are lacking. Modeling supports the understanding of the CB as a case of σ -hole bonds [3]. Halogen Bond (XB) also belongs to the family of σ -hole interactions. A decisive contribution to the stereoelectronic understanding of the XB was given by computational studies on the distribution of the electron density in halogen atoms. These studies demonstrated the anisotropic charge distribution on halogen atoms forming one covalent bond and paved the way to the definition of the σ -hole: a region of depleted and often positive electrostatic potential on the surface of halogen atoms. We based our strategy to investigate CB on this robust experimental background available for XB, the parent interaction of the family. Taking into account the mindset promoted by XB, we designed a series of thiazolium/selenazolium-containing molecules, as models to study CB in systems of increasing structural and functional complexity (Fig. 1). These systems are chosen in order to profile the interactional landscape accessible to molecules important in biological systems and as molecular materials. Specifically, these model compounds are expected to give information of the preferred interactions formed, among others, by Thiamine (Fig. 1, vitamin B1) and related cofactors, by Thioflavin T, a standard dye for amyloids structures, and by thiazolium/ selenazoliun-containing cyanine dyes. Close contacts between sulphur/selenium and an electron-donor group will be discussed in several systems, thiamine and cyanine dyes included, as bona fide cases of CBs.

Fig. 1 – Crystal structures of thiamine monophosphate (right) and two model compounds showing the presence of CBs between the sulphur atom of thiazole ring and neutral and/or anionic electron-donors.



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Keywords: Chalcogen bond, Crystal engineering, σ -Hole interactions

MS30-O4

Chalcogen and halogen bonding in case of multiple i...i and i...s interactions with ambiguous mutual orientations

Irina Yushina1, Natalya Tarasova2, Ekaterina Bartashevich1

- 1. Laboratory of Multiscale modelling of multicomponent materials, South Ural state University, Chelyabinsk, Russia
- 2. Theoretic and applied chemistry, South Ural State Univ ersity, Chelyabinsk, Russia

email: iushinaid@susu.ru

The question of identification and characterization of noncovalent interactions lies in the center of modern crystal engineering problems. Ambiguity of geometric criteria generates the necessity to use electronic descriptors in cases with competitive interactions or unobvious orientation of nucleophilic and electrophilic sites of interacting atoms in molecule and crystals.

In this study we demonstrate several examples of multiple I...I and I...S interactions and test reliability and visibility of the series of electronic criteria. Organic crystals with polyiodide anions and S,N-containing heterocyclic cations open possibility for the design of wide row of nonlinear optical and semiconductor materials as well as dye-sensitized solar cell devices. Variety of crystal structures, available for material engineering is due to the ability of sulfur and iodine atoms form different types of noncovalent interactions, organized in various types of 3D structure motives: nets, layers, chains, cages.

Our computational approach includes solid state quantum-chemical calculations with periodic boundary conditions and atomic basis sets, implemented in CRYSTAL14 package. Electronic criteria based on characteristics of calculated electron density such as ELF distribution and superposition of atomic basin boundaries in the electron density and electrostatic potential are used (TOPOND14).

Testing these computational tools on the series of boundary cases, different types of mutual orientations of interacting atoms can increase reliability of these criteria. The central point of the work is the demonstration of possibility of computational approaches to elucidate which of the interacting atoms acts as acceptor and which as a donor and thus to assign the type of interaction: halogen or chalcogen bond.

In the unusual orientation of I–CH₂ fragment so that equatorial part of iodine atom is directed towards σ -hole region of triiodide anion leads to the situation where iodine atom of organic cation acts as the donor and acceptor of the halogen bond simultaneously. ELF distribution in the plane, containing multiple covalent interactions allows indicating the type of bonding and visualizing features of electron shells distortion due to formed noncovalent interactions. Here we discuss features of σ -hole interactions and their impact on crystal packing and properties of the polyiodide structures.



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Keywords: halogen bonding, chalcogen bonding, organic polyiodides

MS30-O5

Halogen, chalcogen and pnictogen bonding: other bricks in the wall

Peter A. Wood1, Andrew G. P. Maloney1

1. The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, United Kingdom

email: wood@ccdc.cam.ac.uk

The understanding of the relative importance and effect of intermolecular interactions in the solid state is highly valuable in a range of applied research areas, not least in the pharmaceutical industry where control of polymorph stability is crucial. Within pharmaceutical crystal structures, hydrogen bonding tends to dominate - for these interactions there are already a range of established methodologies [1,2] to help understand the most probable outcomes and assess the stability or risk of polymorphism. How important in this context are other intermolecular interactions though? What is likely to be the effect of halogen bonds, chalcogen bonds or pnictogen bonds? This presentation will review the statistics on some typical halogen, chalcogen and pnictogen bonds in the CSD in the context of other intermolecular interactions in organic crystals. We focus on the impact of these interactions for an organic crystal designer or engineer. There are nearly a million structures in the CSD - what do they tell us about the significance of these interactions and do we have enough data?

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MS31 The role of supramolecular interactions in polymorphs and co-crystals

Chairs: Dr. Laszlo Fabian, Prof. Mino R. Caira

MS31-01

Fingerprinting the solid state assembly of cyclic peptoids: solvatomorphic behavior & sorption properties

Consiglia Tedesco¹, Giovanni Pierri¹, Eleonora Macedi¹, Francesco De Riccardis¹, Irene Izzo¹

 Dept. of Chemistry and Biology "A. Zambelli" - University of Salerno, Fisciano, Italy

email: ctedesco@unisa.it

Biological processes rely on control of the dynamic behaviour of biomolecules, the intrinsic flexibility of proteins enables accurate guest recognition and specific substrate conversion. Cyclic peptoids for their biostability and potential diversity seem to be the ideal candidates to evoke biological activities and novel chemical properties both in solution and in the solid state.

Peptoids differ from peptides in the backbone position of the side chains, which are attached to the nitrogen atom. Due to the lack of the amide proton, CH···OC hydrogen bonds, CO···CO and CH-pi interactions play a key role in the solid-state assembly of cyclic *a*-peptoids: face to face or side by side arrangement of the macrocycles mimick *b* -sheet secondary structure in proteins. We also demonstrated that side chains may act as pillars, extending vertically with respect to the macrocycle plane, inducing the columnar arrangement of the peptoid macrocycles (Tedesco et al., 2014).

Recently, we reported that a cyclic hexapeptoid strategically decorated by propargyl and methoxyethyl side chains undergoes a reversible single-crystal to single-crystal transformation upon guest release/uptake involving a drastic conformational change. The extensive and reversible alteration in the solid state is connected to the conspicuous movement (more than 110°) of two propargyl side chains that generate new stabilizing CH-pi interactions with the formation of an unprecedented reversible "CH-pi zipper", which reversibly opens and closes, thus allowing for guest sensing (Meli et al., 2016).

These findings prompted us to perform a polymorph screening of the peptoid compound with a view to understanding the role of the crystallization solvent in the solid state assembly (Macedi et al., 2017).

Here we will explain how the observed extensive solvatomorphism is related to the peculiar conformational flexibility of the peptoid macrocycles and to the role of the solvent molecules in the early stages of nuclei formation. We will visualize the supramolecular architecture of the obtained crystal forms by using Hirshfeld surface analysis and PIX-EL energy calculations to compute the intermolecular interaction energies. We will also show how the solid state assembly of the macrocycles determines the peculiar sorption properties as highlighted by *in-situ* single crystal X-ray diffraction and high resolution X-ray powder diffraction studies.

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Keywords: cyclic peptoids, solvatomorhism, sorption properties

MS31-O2

The role of supramolecular interactions in the formation of isostructural and polymorphic structures

Petra Bombicz1

 Research Centre for Natural Sciences, Hungarian Academy of Sciences, Budapest, Hungary

email: bombicz.petra@ttk.mta.hu

The non-covalent interactions have an influence on seeding and crystal growth, recognition processes, the packing arrangement and the molecular conformation, as well as they affect the stability of the crystal and the biological activity of the compounds.

Both polymorphism and isostructurality are strongly related to intermolecular interactions and crystal symmetries [1]. Structures with similar chemical content may be isostructural. The difference can be in the substitution of the molecule(s) or in the guest molecule in inclusion systems. But how far can a crystal structure tolerate small molecular changes? The molecular conformation of flexible molecules may adjust to the altering supramolecular features in the crystal lattice accompanying chemical changes. It is a subject of debate how far two similar crystal structures can be different to consider them as isostructural. Nevertheless, a higher crystal symmetry can be sacrificed to achieve a better supramolecular arrangement resulting in a lower crystal symmetry, that is, resulting in the introduction of pseudosymmetry and, with that, $Z^> 1$ crystal packing.

The identity of the supramolecular interactions does not ensure isostructurality. On the other hand the occurrence of common crystal packing patterns amongst polymorphs is frequent.

Partial isostructurality may explain the macroscopic behaviour of compounds revealing molecular structure-macroscopical property relationships. Epitaxial crystal growth of compounds becomes possible at a surface where two-dimensional isostructurality is realized, enabling the further growth of the supramolecular pattern in that direction.

A special aspect is the intergrowth of domain arrangements within crystals including varying supramolecular pattern and/or symmetries at the domains' surface having a variable domain proportion resulting in crystals with structurally continuously altering polymorphs and thus in crystals which possess continuously varying physico-chemical properties.

Recognition of the structural features, the supramolecular and symmetry aspects of isostructurality and polymorphism contributes to the proficiency of synthon engineering, the manipulation of the intermolecular interactions, and which makes it possible to engineer crystals.

Acknowledgement:

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Keywords: supramolecular interactions, polymorphism, isostructurality

MS31-O3

Cocrystallisation enhanced optical properties of organic materials – quantum crystallography meets crystal engineering

Marlena Gryl¹, Tomasz Seidler¹, Anna Krawczuk¹, Katarzyna Ostrowska¹, Katarzyna Stadnicka¹

1. Faculty of Chemistry, Jagiellonian University, Kraków, Poland

email: gryl@chemia.uj.edu.pl

During the last decade optical materials have experienced a rebirth of scientific interest. This phenomenon can be explained by the rapidly developing fields of optoelectronics and overall minimization in telecommunication devices. The need for more efficient, stable, and low price materials promotes multicomponent and multifunctional systems over those with single component and single functionality. Additionally usage of more than one building block in a single material enables both steering of the crystal symmetry towards a specific property and at the same time gives means for enhancing the desired physical and/or chemical effect. Co-crystallization is a widely used technique in materials science to obtain materials with modified physiochemical properties or enforce particular crystal symmetry.

Here we present our approach towards crystal engineering of optical materials¹. Birefringence, second harmonic generation, absorption and/or fluorescence can be modified through controlled cocrystallisation of suitable building blocks: one to guarantee a substantial property at the molecular level (suitable chromophore) and the second one selected for controlling crystal symmetry. Combination of quantum crystallography techniques aimed towards analysis of intermolecular interactions (QTAIM², NCI index³) were used alongside with calculations of molecular and bulk properties of the studied systems. Theoretical methodology was supported by measurements of the selected optical properties of the obtained materials.

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Keywords: cocrystallisation, optical materials, crystal engineering

MS31-O4

Influence of the hydrogen bond donors and acceptors ratio on the co-crystals formation features: the case of benzamide derivatives with dicarboxylic acids

Aleksey Manin¹, Ksenia Drozd¹, Andrei Churakov², German Perlovich¹

- Department of Physical Chemistry of drugs, G.A. Krestov Institute of Solution Chemistry of the Russian Academy of Sciences, Ivanovo, Russia
- Department of Crystal Chemistry and X-ray Structure Analysis, Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow, Russia

email: alexnmanin@gmail.com

Co-crystals are multicomponent crystals that consist of two or more neutral molecules interacting with each other through non-covalent interactions. Co-crystals are well established in the literature as a route to new and alternative solid forms, and a promising method for fine-tuning properties of a molecule. The design of new co-crystals requires an understanding of hydrogen bonding functional groups and the supramolecular synthons between the drug and the coformer. Synthons are sub-classified as homosynthons and heterosynthons, i.e. those between like and unlike functional groups, respectively. There are many design strategies for binary cocrystals as seen from the literature. A crystal engineering or supramolecular synthon-based approach is a convenient and common method used in the design of such systems, implementing frequently occurring motifs from the literature applicable to the functional groups present in the API of interest. [1]

Tothadi with coauthors published a series of papers devoted to the study of synthon modularity in binary and ternary co-crystals of benzamide derivatives with dicarboxylic acids. [2, 3] The authors suggested that dicarboxylic acid can be introduced between the molecules of the benzamide derivatives bound through the amide-amide homosynton to realize the packaging of the single-component diphenol crystal. Indeed, the theoretical strategy allowed the modularity of the synthons to be used to produce a series of co-crystals with 4-hydroxybenzamide in a stoichiometric ratio of 2:1. [2]

In our work, we continued the studies of Tothadi and tried to analyze how the additional donor of the hydrogen bond in the benzamide molecule will affect the packing of the co-crystals with dicarboxylic acids. 4-aminobenzamide was chosen as the object of the study. It should be noted that the molecule of 4-aminobenzamide has not been studied well in the context of crystal engineering yet. Just four hits can be seen in the CSD corresponding to the pure compound and three cocrystals.

Seven new co-crystals and salts of 4-aminobenzamide with dicarboxylic acids and one new co-crystal of 4-hydroxybenzamide with malonic acid were obtained, monocrystals were grown and their crystal lattices were solved. DSC measurements were conducted to investigate the thermal behavior of BZA derivatives (4-AmBZA and 4-OHBZA) salt/cocrystals. The Xpac analysis was made for 34 known cocrystals of the p-derivatives of BZA. The similar "supramolecular constructs" of studied molecules crystal structures were identified and the similarity of molecular packs was quantified.

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Keywords: aminobenzamide, intermolecular interactions

MS31-05

Large family of halogen-bonded cocrystals involving CoCl₂L₂ building blocks

Dominik Cinčić1, Katarina Lisac

 Department of Chemistry, Faculty of Science, University of Zagreb, Zagreb, Croatia

email: dominik@chem.pmf.hr

An overwhelming majority of reported studies and strategies for incorporating metals into halogen-bonded architectures have focused on single component metal-organic solids which include the formation of metal-organic complexes using ligands with pendant halogen bond donor groups (e.g. acetylacetonate derivatives or halopyridines) [1,2]. On the other hand, synthesis of multi-component metal-organic materials with organic halogen bond donors has received much less attention. Most reports on such materials have focused on the formation of ionic structures involving metal complexes with simple inorganic ligands (e.g., Cl-, CN-, SCN- etc.) and cations as halogen bond donors (e.g. halopyridines) [1,2]. Much less explored systems are neutral metal-organic cocrystals. Few approaches have been presented as promising and they have generally been focused on cocrystals of neutral halogen bond donors and metal complex subunits with pendant acceptor groups: halogen atoms [3], chelating ligands such as imines and acetylacetonate derivatives [4,5], neutral molecules coordinated to metal centre such as morpholine or thiomorpholine [6]. Following our previous study where we described the halogen bonding proclivity of the chlorine atom coordinated to the Co(II) metal centre, in this work we demonstrate a strategy for synthesis of halogen-bonded metal-organic cocrystals by utilizing metal complexes whose pendant chloride group enables halogen bonding [7]. A series of 12 cocrystals involving octahedral CoCl₂L₂ complexes [L = 2,2]bipyridine (1) or 1,10 phenantroline (2)] as halogen bond acceptors were prepared by both liquid-assisted grinding and conventional solution-based methods. The efficacy of this strategy is evident by the assembly of a large family of cocrystals involving six perfluorinated halogen bond donors: 1,4-diiodotetrafluorobenzene (14tfib), 1,3-diiodotetrafluorobenzene (13tfib), 1,2-diiodotetrafluorobenzene (12tfib), 1,3,5-triiodotrifluorobenzene (135tfib), iodopentafluorobenzene (ipfb) and octafluoro-1,4-diiodobutane (ofib). Single crystal X-ray diffraction experiments have shown that cocrystals display different crystal packing, governed by Cl...I halogen bonds involving halogen bond donor iodine atoms and metal complex chlorine atoms (varying from 3.061 to 3.471 Å). The monotopic donor ipfb and ditopic donor 12tfib form discrete 2:1 or 1:1 halogen bonded complexes with both acceptors. The exception is 12tfib which, with 1, acts as both monotopic and ditopic donor thus forming two cocrystals, 2:1 (discrete complex) and 1:1 (chains). The halogen bond motifs in cocrystals based on 14tfib, 13tfib, 135tfib and ofib exhibit higher dimensionality, halogen bonded chains. The exceptions are two cocrystals of 1, one with 13tfib forming a two-dimensional layered halogen-bonded structure, and with ofib forming a three-dimensional halogen-bonded structure.

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Keywords: Halogen bonding, Cocrystals, Coordination compounds

MS32 Molecular recognition and crystal engineering

Chairs: Dr. Berta Gómez-Lor, Prof. Delia Haynes

MS32-O1

The many lives of resorcinarene cavitands: from molecular recognition to crystal engineering

Chiara Massera¹, Roberta Pinalli¹, Francesca Guagnini¹, Alessandro Pedrini¹, Enrico Dalcanale¹

1. Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Parma, Italy

email: chiara.massera@unipr.it

Since their first appearance on the chemistry scene thirty years ago [1], resorcinarene-based cavitands have been exploited both as receptors for molecular recognition and as building blocks for crystal engineering [2]. Their versatility primarily stems from the possibility of choosing different bridging groups to connect the phenolic hydroxyls of the resorcinarene scaffold. This allows the tuning of the shape, dimension and complexation properties of the cavity, which can thus interact with neutral and charged molecules through H-bonding, $\pi \cdots \pi$ stacking and CH $\cdots \pi$ interactions, but also form coordinative bonds with metal centers to create discrete complexes, cages or extended networks.

We present our recent investigations on various functionalised quinoxaline-bridged cavitands for molecular recognition (see figure below) and phosphonate cavitands as ligands for the formation of coordination compounds



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Keywords: cavitands, host-guest interactions, coordination compounds

MS32-O2

Close contacts involving carbon and antimony: Tetrel bonded and pnictogen bonded systems by design

Giuseppe Resnati¹, Patrick Scilabra¹, Vijith Kumar¹, Giancarlo Terraneo¹

 Laboratory of Nanostructured Fluorinated Materials (NFMLab), Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Via L. Mancinelli 7, 20131, Milano, Italy

email: giuseppe.resnati@polimi.it

In this communication we will describe the packing of some homomeric and heteromeric crystals wherein the composition and architecture is affected and/or determined by attractive interactions involving carbon and antimony atoms as electrophilic sites. Molecular modelling predicts that region(s) of depleted electron density are typically present on an atom opposite to the covalent bond(s) it is involved in. This is true for any element belonging to groups 14-18 of the periodic table [1] and the electrostatic potential at the depleted region(s) becomes positive when the atom is covalently bonded to strongly electron withdrawing residues [2]. We thus expected that the depleted regions on fluorinated carbon and antimony moieties might be positive enough to enable for the formation of attractive interactions with lone pair possessing atoms. We also expected that the resulting bonds might be strong enough to determine the crystal composition and architecture. Here we describe that various 5.5-difluorobarbituric derivatives form adducts were F-C-O=C intermolecular contacts can be as short as 90% of the sum of carbon and oxygen van der Waals radii. The C…O supramolecular synthon in these derivatives is robust enough to be observed also in 5,5-dichloro and 5,5-dibromo analogues, namely when halogens less electron withdrawing than fluorine are present (Fig. 1). As to fluorinated antimony derivatives, we report, for instance, that the tendency of antimony trifluoride to attractively interact with lone pair possessing atoms is so strong that in the tetrameric adducts formed on self-assembly with p-dipyridyl dioxide, two antimony atom gives two F-Sb--O close contacts with two different dioxide molecules. The described interactions are typically named tetrel bond and pnictogen bond [3], respectively. The reported results shown how their understanding is developed enough to enable for their successful use in the design of the intermolecular interactions of crystal lattices. The described structure may also suggest that tetrel bond and pnictogen bond are robust enough to become new, useful and general tools in crystal engineering.

Fig. 1 Adducts present in crystals of 5,5-difluoro- (left), 5,5-dichloro- (mid), and 5,5-dibromo-N,N'-dimethylbarbituric acid (right); F–C···O=C tetrel bonds are dashed black lines.



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Keywords: Tetrel bond, Pnictogen bond, Crystal engineering

MS32-O3

Is it usual to be unusual? - An investigation into Molecular Conformations in Organic Crystals

S. E. Wright¹, M. Bryant², R. J. Davey¹, A. J. Cruz-Cabeza¹

- School of Chemical Engineering and Analytical Science, University of Manchester, Manchester, United Kingdom
- 2. Cambridge Crystallographic Data Centre, Cambridge, United Kingdom

email: sarah.wright-6@postgrad.manchester.ac.uk

The molecular complexity and size of novel drug molecules is ever increasing, and so is their conformational flexibility. Complex flexible drug compounds may often be challenging to crystallise. Crystallisation is the final step in the manufacture of active pharmaceutical ingredients and with over 90% of pharmaceuticals being crystalline it is important to understand and control this process. The poor crystallisation behaviour of flexible molecules has been linked to the conformational diversity found in solution [1]. In solution, conformers are in equilibrium and their relative populations depend on their relative stabilities. If a crystal conformation is similar to that of a stable conformer in solution, no conformational change or adjustment would need to occur for the system to nucleate and grow [2]. However, if the crystal conformation corresponds to a highly distorted conformer or a higher-energy conformer, then significant conformational adjustment or change would need to occur during crystallisation [3]. Such conformational changes and adjustments may limit crystal growth and are the subject of the present research.

We have investigated the occurrence of unusual conformations in the Cambridge Structural Database (CSD) for various subsets of molecular crystals. Torsion angles in flexible molecules were classified as being "unusual" when they were observed in less populated areas of the CSD torsion distributions. We then investigate the conformational energy landscape of these molecules crystallising with unusual torsions. How usual is it to be unusual? Do these "unusual" torsions relate to high-energy conformations? How much conformational distortion is required for some molecule to crystallise? What causes these torsions to become unusual? Are certain torsions more prone to distortion and change? This contribution attempts to answer all of these questions by providing new insightful data on the effect of crystal structure on conformations.

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Keywords: Molecular Conformation, Energy, Crystallisation

MS32-O4

Understanding selectivity in host-guest systems

luigi Nassimbeni1

1. Chemistry, Rondebosch, South Africa

email: luigi.nassimbeni@uct.ac.za

The formation of inclusion compounds, comprising host and guest molecules, depends on the phenomenon of molecular recognition. An important application of this process is the separation of compounds in a mixture, particularly when the individual components have similar physico-chemical properties as often occurs in isomers.

The techniques which may be used to understand the mechanism of separation are:

a) Competition experiments, b) Crystal Structure, c) Thermal Analysis; d) Packing coefficient; e) Hirshfeld Surface Analysis; f) Lattice Energy

Each of these methods will be outlined, and recent publications dealing with important aspects will be indicated. Recent experimental results of guest selectivity and the concomitant mechanisms will be presented.

Keywords: Host-Guest, Selectivity, Mechanism

MS32-O5

Finding polar crystal structures: molecular structures, intermolecular interactions and unit cell dipoles

Frank Blockhuys1, Jasper Van de VeldeAlain Colla2

- 1. Department of Chemistry, University of Antwerp, Antwerp, Belgium
- 2. Crystallization Technology Unit, Johnson & Johnson , Beerse, Belgium

email: frank.blockhuys@uantwerpen.beT

The structure and electronic properties of one class of organic semiconductors, i.e., 1,4-distyrylbenzene (1,4-DSB) and its derivatives, have been extensively studied, indicating the usefulness of the DSB template for electro-optical materials [1]. A number of their applications, such as non-linear optics and non-volatile organic memories, require materials with dipole moments, both at the molecular and the supramolecular levels. These two requirements, however, generally work against each other: 1,4-DSBs containing electron acceptor (A) and donor (D) fragments connected by a π -spacer (A- π -D structures) have large molecular dipoles and superior molecular properties, but will, in the majority of the cases, result in the energetically preferred anti-parallel dipolar stacking in the crystal leading to a centrosymmetric and, therefore, non-polar supramolecular structure. These observations have led to the development of a rational overall design strategy for polar molecular crystals of DSB-type oligomers, consisting of four parts. First, the formation of an anti-parallel stacking should be hampered by the introduction of steric hindrance between the molecules; this could be obtained by deviating as much as possible from rigid-rod molecular shapes. Second, the electronic-ground-state dipole moment of the molecules should be sufficiently small; this way, the energy barrier to stack two molecules with aligned dipoles is lowered and the probability to obtain a non-centrosymmetric arrangement in the resulting solid is increased. Third, the deviation from planarity of the constituent molecules should be increased through the incorporation of heteroatoms in the conjugated spacers between the rings; the introduction of (a) nitrogen atom(s) results in typical non-planar molecular shapes hampering the formation of π -stacks [2]. Fourth, the most favourable conformation of the molecule should have an energetic advantage with respect to its other conformations which is as high as possible; this results in greater control over which conformation is eventually found in the solid and, consequently, its shape and the size of its dipole moment. The results of a CSD analysis reveal that 1,4-DSBs are statistically far less prone to crystallization in polar space groups than 1,3-DSBs and our efforts are now focused on developing new materials using the latter template in an approach which combines synthetic and computational chemistry, and crystallography. Computational chemistry is used to great advantage, from the calculation of molecular properties such as conformational energies and dipole moments to full DFT treatments of the molecular crystal, and an elegant procedure has been developed for the calculation and visualization of unit cell dipoles.

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Keywords: Polar Crystals, Intermolecular Interactions, Unit Cell Dipoles

MS33 Prediction of molecular crystal structures

Chairs: Dr. Jacco van de Streek, Dr. Aurora Cruz-Cabeza

MS33-01

Computational screening for organic drug hydrates

Doris Braun¹

1. University of Innsbruck / Institute of Pharmacy, Innsbruck, Austria

email: doris.braun@uibk.ac.at

Water has the ability to occupy regular positions in the crystal lattice of other substances and to form molecular compounds, named hydrates. As water is an ever present component of the environment such multi-component crystals can form during many steps of product manufacturing and can have profound effects on the performance of a (drug) product. [1] Hydrate formation is a widespread phenomenon and is known to occur for at least one third of drug molecules. [2] Nevertheless, we are still not able to predict hydrates, their stability and dehydration mechanisms based on the molecular diagram only. With computational crystal structure prediction (CSP) methods being successfully employed for predicting smaller pharmaceutical molecules and even multi-component systems, [3] we tested the potential of CSP for drug hydrates. Stoichiometric and nonstoichiometric hydrate systems were chosen as model compounds for experimental and computational studies.

The experimental screen of two dihydroxybenzoic acid (DHB) isomers indicated hydrate formation for one isomer but not the other. The computationally generated hydrate crystal energy landscapes correctly predicted hydrate formation for 2,4-DHB and its stoichiometric ratios and rationalised why no hydrate was found for 2,5-DHB [4].

For 4-aminoquinaldine (4-AQ) the computational hydrate screening suggested the existence of an unknown monohydrate polymorph, which was then produced and found to be the thermodynamically most stable hydrate form of 4-AQ. [5] Calculating the crystal energy landscapes for hydrates is very complex and computationally (time) demanding, as host and different guest molecules in different stoichiometric ratios have to be considered. Therefore, we tested whether it is possible to derive information about hydrate formation for a Z'=3 monohydrate and higher hydrates from their Z'=1 hydrate and anhydrate crystal energy landscapes, respectively. For o-phenanthroline the Z'=1 monohydrate the crystal energy landscape rationalised why the compound forms a very stable Z'=3 channel hydrate. [6] For the hydrate forming alkaloid brucine and the non-hydrate forming derivative strychnine the evaluation of the anhydrate crystal energy landscapes, in particular the close-packed crystal structures and high-energy open frameworks containing voids of molecular (water) dimensions, allowed us to unravel the diverse solid state behaviour of the two alkaloids at a molecular level. [7]

Thus, modelling at the electronic and atomistic level can provide vital support for unravelling the complexity of organic hydrate systems and in particular adds confidence to the interpretation of the experimental data.

Keywords: hydrate, crystal structure prediction



Computation-led discovery of functional molecular materials

Graeme Day¹

1. Chemistry, Southampton, United Kingdom

email: g.m.day@soton.ac.uk

The design of molecular crystals with targeted properties is the goal of crystal engineering. However, our predictive understanding of how a crystal's properties relate to its structure, and how crystal structure in turn relates to molecular structure, are not yet sufficiently reliable to confidently design functional materials. One reason for this is that the crystal structure adopted by a molecule is rarely determined by a single, predictable structure-directing interaction, but typically results from a balance of many relatively weak intermolecular interactions. It is, therefore, common for a molecule to have many nearly equi-energetic possible crystal structures, with the best structure (the global lattice energy minimum) favoured by only a few kJ mol-1 or less over alternative structures that might have very different physical properties. This existence of competing low energy crystal structures is related to the prevalence of polymorphism in molecular crystals, as well as the observation that small changes to chemical structure can lead to dramatic changes in crystal packing.

Computational methods for crystal structure prediction (CSP) have been developed to help anticipate the crystal structure that a molecule will form. These methods are based on a global search of the lattice energy surface and a ranking of local energy minima according to their calculated relative stabilities. Each of the crystal structures in the resulting ensemble encodes a set of properties, many of which are calculable using computer simulations. This talk will discuss how the set of predicted structures, their calculated energies and simulated properties, which we present as an energy-structure-function (ESF) map, can be used to guide experimental programmes for materials discovery. The ESF mapping approach will be illustrated with its use in the discovery of unprecedented porous molecular crystals[1] and its application to organic semiconductors[2,3].

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Keywords: crystal structure prediction, materials discovery, functional materials

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MS33-O3

Accurate and efficient representation of intramolecular energy in ab initio generation of crystal structures. Part II: Smoothed Intramolecular potentials

Isaac Sugden1, Claire Adjiman1, Costas Pantelides1

1. Chemical Engineering, London, United Kingdom

email: I.sugden@imperial.ac.uk

The CrystalPredictor¹ and CrystalOptimizer² codes have been used to explore the space of crystal structures successfully in several crystal structure prediction (CSP) investigations in recent years, including in the series of blind tests organised by the Cambridge Crystallographic Data Centre and in the prediction of the crystal structures of pharmaceutically-relevant molecules. One of the key research challenges in developing CSP capabilities is to enable the investigation of increasingly flexible compounds within tractable computational times, competitive with experimental polymorph screens.

We present recent advances in CrystalPredictor that are focussed on addressing this challenge. Specifically, we discuss the smoothing of the intramolecular potential,³ an innovation in CrystalPredictor II that allows the most efficient use of computational effort to cover a flexible molecule's conformational space. This improvement achieves greater accuracy in the initial ranking of potential crystal structures, while managing computational cost, so that a thorough exploration of the search space is possible. We present CSP results for the highly polymorphic NSAID drug Flufenamic acid to demonstrate this capability, with a \approx 30% increase in the efficiency of the global search stage, alongside increased confidence in the final polymorphic landscape.

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Keywords: Crystal Structure Prediction, polymorphism, computational chemistry

MS33-O4

Phase diagram prediction by data mining via temperature-dependent force fields

Detlef Hofmann1, Liudmila Kuleshova2

1. CRS4 - FlexCryst, Pula, Italy 2. FlexCryst, Uttenreuth, Germany

email: dwmhofmann@aol.com

Modern force fields are accurate enough to describe thermal effects in molecular crystals. We applied the recently developed temperature-dependent force field (1) to predict the transition temperature for polymorphs. An estimation of the transition temperature of paracetamol demonstrated the possibility for prediction using the temperature-dependent force-fields.

The earlier approach of force fields for finite temperatures (2) is extended to a force field with a continuous function for the temperature. In this model the intermolecular potentials are described by effective atom pair potentials. Each atom pair potential is developed as Taylor series of $1/r^3$. The Pauli repulsion is extended by a temperature dependency: $1/r^{12} \rightarrow (1+alpha)/r^{12}$. For the parametrisation of the force field we used Data Mining on experimental structures (3) with the temperature as an additional descriptor. The temperature-dependent force field can be used as for the energy minimization at a finite temperature and for molecular dynamics, which requires zero-K potentials.

The parameters of the model have been obtained by training on 21,095 experimental crystal structures for hydrogen bonds in oxygen and nitrogen compounds. The force field is validated for the prediction of crystal density, temperature density gradients and transition temperature. The crystal density prediction was validated by minimization of all non-ambient crystal structures available in The Cambridge Structure Database. The mean error is halved by taking the temperature into account. We estimated the thermal density gradients of several organic crystals with experimental data of one substance at various temperatures. The error of the predictions varied from 0 to 29 %. Finally, a prediction of the transition temperature of paracetamol demonstrated the possibility for prediction phase diagrams.

In the abstract image the two polymorphs of paracetamol under investigation are shown. The orthorhombic modification (form II) transforms at 385 K to the monoclinic polymorph (form I) with the half cell volume.



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Keywords: Crystal Structure Predtion, Data Mining, Force Fields

MS33-05

X-ray diffraction data as a source of information of vibrational contribution to enthalpy and entropy of polymorphic systems

Anna Hoser1, Philip Miguel Kofoed2, Anders Ø. Madsen2

- 1. Chemistry Department, University of Warsaw, Warsaw, Poland
- 2. Department of Chemistry, University of Copenhagen, Copenhagen, Denmark

email: annahoser@chem.uw.edu.pl

The stability of crystals at a given temperature is determined not by the lattice energy, but by Gibbs free energy. Thus, to compare stabilities of polymorphs at given temperature beside lattice energy, one should take into account contributions from vibrational enthalpy, entropy and zero point energy. Those contributions can be calculated by means of DFT methods, but, as they require supercell calculations, they have high computational costs.

An idea of estimating entropy from X-ray diffraction data is not new - in 1956 Cruickshank [1] estimated entropy of crystalline naphthalene by means of TLS analysis from ADPs from single crystal X-ray diffraction data. In 1989 Jack Dunitz and co-workers used a similar approach to estimate the entropy of conformational polymorphs of dimethyl-3,6-dichloro-2,5-dihydroxyterephthalate [2]. Dunitz et al was able to explain the mechanism of phase-transformation based on an analysis of the Debye-Waller factors, but their results contradicted the well-established thermodynamic order of stability of the systems. They write:

"Why has our intuition led us astray in expecting that the crystal with the larger atomic ADP's should have the greater entropy?"

We decided to reinvestigate this particular polymorphic system with normal mode refinement, which enables the refinement of frequencies of normal modes obtained from *ab-initio* periodic computations at Γ point, against single crystal diffraction data. Frequencies obtained from *NoMORe* can be used to estimate thermodynamic properties – heat capacity and vibrational contributions to entropy and enthalpy [3].

In order to conduct *NoMoRe* refinements we collected new high-quality single crystal X-ray diffraction data for polymorphs and we conducted DFT theoretical calculations of frequencies at Γ point and a reference supercell calculations. Estimates of the frequencies of acoustic modes, obtained after *NoMoRe* are in very good agreement with those from supercell calculations. Based on the *NoMoRe* analysis, we can predict, that white form is stable at high temperature range, and yellow at low temperature range, which is in agreement with experimental results. By discussing contributions from low and from high frequency modes to vibrational entropy and enthalpy we are able to explain the important question which was raised by Dunitz et al.



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Keywords: polymorphism, lattice dynamics

MS34 Exploring structural dynamics in crystals

Chairs: Dr. Pance Naumov, Prof. Leonard Barbour

MS34-01

From reactivity of solids to high-pressure crystallography and back: response of molecular crystals to mechanical stress

Elena Boldyreva1

 Novosibirsk State University, Chair of Solid State Chemistry, Novosibirsk, Russia

email: eboldyreva@yahoo.com

The contribution gives a survey of the research that has been carried out through over several decades. Any reaction in a crystal is accompanied by generating stress. The manifestations of this stress are elastic and plastic strain and fragmentation. As a reaction proceeds, the mechanical stress that arises in the crystal can have a significant influence on the subsequent transformation. This phenomenon is termed as feed-back, which can be either positive, or negative. One can introduce the concept on "chemical pressure", to describe the reaction in the crystal which is stressed by the reaction itself. In selected cases the mechanism of the reaction in relation to the mechanical response of crystals can be studied in detail. I illustrate this, using selected examples of reactions in molecular crystals. The effects of "chemical pressure" can be compared with those of strain imposed by hydrostatic compression. Modern high-pressure crystallography makes it possible to follow even subtle changes in molecular geometry and intermolecular interactions. I discuss structural distortion induced by high pressure and structural transformations, in a comparison with strain and structural transformations accompanying chemical reactions in the same crystal. Eventually, we consider the chemical reactions induced by irradiation or heating if occurring in the hydrostatically compressed crystals.

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Keywords: mechanical stress, pressure, reactivity of solids

MS34-O2

Photomechanical and thermomechanical molecular crystals

Takuya Taniguchi1, Hideko Koshima1

 Research Organization for Nano & Life Innovation, Waseda University, Tokyo, Japan

email: s092821627@ruri.waseda.jp

Crystals that can respond to external stimuli, such as light and heat have increasingly attracted attention in chemistry, materials science, and soft robotics fields. Most of photomechanical crystals exhibit bending and expansion/contraction motion. We have already developed several photomechanical bending processes of azobenzene, salicylideneaniline, and other crystals. Recently, we have reported walking and rolling locomotion of chiral azobenzene crystals, induced thermally by phase transition. The photomechanical and thermomechanical crystals are introduced and discussed in this conference.

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Keywords: Photomechanical Bending, Thermomechanical Locomotion, Mechanisms

MS34-O3

Watching chemistry happen – dynamic studies on light induced transformations in linkage isomerism complexes

Mark Warren¹, Lauren Hatcher², Jonathan Skelton², Paul Raithby², Dave Allan¹

1. Beamline 119, Diamond Light Source, Didcot, United Kingdom 2. University of Bath, Bath, United Kingdom

email: mark.warren@diamond.ac.uk

The investigation of short-lived reaction intermediates and transient species upon light activation in chemical and biological species is of upmost importance to better understand the pathways in a reaction.

Linkage isomers are complexes that contain an ambidentate ligand that can bond to the metal centre through two or more donor atoms. The ambidentate ligand can be switched from one state to another in response to irradiation, and display a change in the bulk properties e.g. reflective index or colour change. At low temperatures these metastable species can be cryo-trapped and the lifetime can last longer than a diffraction experiment, but they can revert back to the ground state as they approach room temperature. The metastable species have a tuneable lifetime depending on temperature.

For metastable species, conventional time-resolved studies using a high intensity pulsed laser proved difficult as the nanosecond pulse induced crystal heating and thus reverted the metastable species back to the ground state. Beamline i19 at Diamond, in collaboration with the Raithby Group at the University of Bath have developed a time-resolved setup with LEDs and a novel collection strategy to investigate species with lifetimes from minutes to milliseconds. The LEDs are able to spread out energy load on the crystal while giving ample intensity for conversion. Utilising the electronic gating capabilities of the Pilatus detector allowed entire time-series to be obtained simultaneously within a couple of hours. Automated processing routines gave fully refined structures minutes after the data-collection completion.



Keywords: dynamics, photocrystallography, linkageIsomers

MS34-O4

Analysis of the dynamics of a jumping crystal with Molecular Dynamics and TLS analysis from powder diffraction data

Jacco van de Streek1

1. Avant-garde Materials Simulation, Merzhausen, Germany

email: jacco.vandestreek@avmatsim.eu

Jumping crystals often shatter as a result of the phase transformation causing their jumping, making it difficult to analyse the structure after the phase transition.

For a compound for which the structure of the low-temperature phase was known from single-crystal analysis but where the disintegration of the crystals during the phase transformation prevented the elucidation of the high-temperature phase, we were able to observe a discontinuity in the unit-cell parameters when the temperature of the low-temperature phase was increased with Molecular Dynamics (MD). The new phase had a higher symmetry than the low-temperature phase and the anisotropic displacement parameters calculated from the Molecular Dynamics trajectory identified strong libration of the molecules as the cause of the phase transition.

Temperature-dependent powder diffraction experiments confirmed the structure of the new phase, but because anisotropic displacement parameters cannot be reliably refined against powder diffraction data, it seemed impossible to verify experimentally that molecular libration caused the phase transition.

This was solved by refining the anisotropic displacement parameters using a TLS (Translation-Libration-Skew) model, reducing the number of parameters required to describe the anisotropic motion of the non-hydrogen atoms by a factor of four. Additionally, the TLS approach allowed us to include the description of the anisotropic motion of the hydrogen atoms, even though only laboratory X-ray powder diffraction data were available. The results from the experimental TLS analysis were an excellent match with the results from the Molecular Dynamics calculations.

The combination of Molecular Dynamics simulations and TLS refinement against XRPD data therefore allowed a full characterisation, at the atomic level, of the anisotropy of the dynamics of the individual molecules leading up to, during and after a phase transition despite the destruction of the single-crystals during the phase transition.

Keywords: TLS, Molecular Dynamics, XRPD

MS34-05

Is single-crystal diffraction a suitable technique to study jumping crystals in situ?

Michele Zema¹, Željko Skoko², Gennaro Ventruti³, Jasminka Popović⁴, Serena C. Tarantino³

- 1. Department of Earth and Environmental Sciences, University of Pavia, Pavia, Italy
- 2. Department of Physics, University of Zagreb, Zagreb, Croatia
- Department of Earth and Geo-environmental Sciences, University of Bari, Bari, Italy
- 4. Division of Materials Physics, Ruđer Bošković Institute, Zagreb, Croatia

email: mz@iucr.org

Thermally induced mechanical properties of crystals, including the thermosalient effect manifested by some crystalline materials that jump many times their own size when heated or cooled, are known since the '80s. Modern analytical techniques have allowed deeper and deeper insights into the transformations that rule this phenomenon, and renewed the interest in a class of mechanically responsive materials that hold potential for a broad range of applications in electronics, soft robotics, regenerative medicine, and related fields [e.g., 1-2].

However, potential applications of the thermal-to-mechanical energy conversion through thermosalient effect require detailed understanding of the structural changes at the atomic/molecular level. This proves to be quite challenging, because of decreased crystal quality, latent/permanent crystal deformations, or simply because of technical difficulties of performing in situ single-crystal X-ray diffraction (SC-XRD) analyses. As a consequence, very few evidences on the atomic-scale mechanisms driving these transitions are available, mainly on non-molecular compounds [e.g., 3].

We have developed a new device and crystal mounting methods that make this technique flexible and fully versatile for studies under different heating (up to ca. 1100°C) and atmospheric conditions, with no limitations to the rotation of goniometer circles. Crystal mounting in quartz vials (in air, in closed atmosphere of virtually any conditions; under vacuum) by making use of quartz wool to avoid mechanical stress on crystal surfaces is compatible with this set-up and proved particularly efficient in the study of jumping crystals, as quartz fibres are flexible enough to accommodate crystal movements at the transition.

We present here the first results on three thermosalient crystals, oxitropium bromide (OTB), scopolamine methyl bromide (SMB) and hydrated SMB (SMBH). In all cases, in situ HT SC-XRD data were collected at regular intervals up to above the transition temperature and down to room temperature. All samples show negative thermal expansion of at least one cell parameter. OTB undergoes a structural transition at 330 K with some hysteresis on cooling. Variation of the unit-cell parameters with T shows a fairly large first-order jump. No discontinuities have been observed in the unit-cell parameters evolution with T for SMB, whereas SMBH clearly shows a sudden jump at ca. 320 K, also in this case reversible and with some hysteresis on cooling. Preliminary structure refinements indicate a single crystal-to-single crystal transformation due to a dehydration/ re-hydration process rather than a phase transition.

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Keywords: thermosalient effect, negative thermal expansion, in situ XRD

MS35 From 0- to 3-dimensional porous systems

Chairs: Dr. Felipe Gandara, Prof. Wendy Queen

MS35-01

Metalorganic frameworks as platforms for biosignaling molecules

Elisa Barea¹, Francisco J. Carmona¹, Carmen R. Maldonado¹, Shuya Ikemura², Carlos C. Romão³, Zhehao Huang⁴, Xiaodong Zou⁴, Susumu Kitawaga⁵, Shuhei Furukawa⁵

- 1. Department of Inorganic Chemistry, University of Granada, Granada, Spain
- Institute for Integrated Cell-Material Sciences, Kyoto University, Kyoto, Japan
- 3. ITQB, Universidade Nova de Lisboa, Oeiras, Portugal
- 4. Berzelii Centre Exselent, Stockholm University, Stockholm, Sweden
- Institute for Integrated Cell-Material Sciences, Kyoto University, Kyoto, Japan

email: ebaream@ugr.es

Since pioneering work of Nobel laureates Furchogtt, Ignarro and Murad concerning nitric oxide (NO) as an important biosignaling molecule in the cardiovascular system, significant attention has been paid on the physiological and potential therapeutic role of NO and other endogenously produced small gas molecules, such as carbon monoxide (CO). The easiest administration route for these gas molecules into the body is the inhalation of their air mixtures. However, this strategy lacks of specificity and, in the case of CO, the higher affinity of this gas to haemoglobin/myoglobin compared to oxygen, as well as its poor solubility in water, means that high doses of inhaled CO are required to obtain a beneficial effect with the concomitant associated safety risk. In order to overcome these drawbacks, CO/ NO-releasing materials (CORMAs and NORMAs) appear as solid CO/NO storage materials able to deliver the corresponding gas in a triggered manner. In this context, one of the most versatile strategies to design new CORMAs/NOR-MAs consists in the use of MOFs as biocompatible vehicles of these therapeutic gases.[1]

Taking into account this background, firstly, we have combined an existing CO-releasing molecule with the biocompatible MOF [Al(OH)(SDC)], (H2SDC: 4,4'-stilbenedicarboxylic acid) (CYCU-3) to obtain a new CORMA. In this work, we have shown the feasibility to control particle size and morphology in CYCU-3 by means of the coordination modulation method. With this aim, we have screened different reagent concentrations and modulator/ligand ratios. As a result, CYCU-3 materials with different particle features have been isolated including a new crystalline phase, for which a structural model based on a squeezed and defective structure of pristine CYCU-3 has been proposed. Besides, the air-stable and photoactive CO-releasing molecule ALF794 (Mo(CNCMe₂CO₂H)₃(CO)₃), which has demonstrated efficacy against acute liver injury in animal models, has been selected to be encapsulated in three selected CYCU-3 materials. Then, the influence of structure,

crystal size and morphology over the resulting CORMAs properties including payload, CO-delivery and matrix stability have been evaluated.^[2] Finally, we have also prepared novel NORMAs improving NO adsorption on the MOF [Ni₈(OH)₄(H₂O)₂(BDP)₆] (H₂DDP=1,4-bis(pyrazol-4-yl) benzene-4) through the sequential introduction of miss-ing-linker defects and extra-framework Fe²⁺ cations in this robust porous structure. In addition, a cation exchange strategy has been used with the same purpose on the cationic biocompatible MOF (NH₂(CH₃)₂)₂[Zn₈(adeninate)₄(BP-DC)₆] (BPDC = 4,4'-biphenyldicarboxylate). The NO releasing ability of these new NORMAs as well as their stability under physiological conditions have been compared.

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Keywords: "CO releasing materials" "NO releasing materials"

MS35-O2

Tuning properties and functionality in modulated crystallisation of high-valent metal-organic frameworks

Ross Forgan¹

1. School of Chemistry, University of Glasgow, Glasgow, United Kingdom

email: ross.forgan@glasgow.ac.uk

Metal-organic frameworks (MOFs) are network materials comprised of organic ligands connected by metal ion clusters into multidimensional structures that often have permanent porosity. Their chemically addressable structures, combined with their ability to store large quantities of small molecules within their pores, have led to applications in gas storage, heterogeneous catalysis, sensing, and drug delivery, amongst others. Coordination modulation, the addition of monomeric modulators to synthetic mixtures, can tune particle size from nanometres to centimetres, through capping of crystallites (decreasing) or coordinative competition with ligands (increasing).

The talk will cover the development of our own modulation techniques for high valent MOFs, and the use of modulation to control physical properties such as interpenetration, defectivity, and porosity. Our techniques provide access to high quality single crystals of many different MOFs, allowing the subsequent characterisation of their mechanical properties,[1] single-crystal to single-crystal postsynthetic modification,[2] development of fluorescent sensors,[3] and sequestration of toxic gases.

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Keywords: metal-organic frameworks, coordination modulation, mechanical properties

MS35-O3

CO_2 adsorption sites in the triangular channels of $Fe_2(BPEB)_3$: an insight by in-situ and operando high-resolution and high-energy PXRD

Simona Galli1, Carlotta Giacobbe2, Elisa Lavigna1, Angelo Maspero1

1. University of Insubria, Como, Italy

2. European Synchrotron Radiation Facility, Grenoble, France

email: simona.galli@uninsubria.it

Growing concerns on global warming stimulate research to reduce anthropogenic CO2 emission and lower atmospheric greenhouse gases concentration. Till the use of greener energy sources will be practicable, CO₂ sequestration technologies will be the most viable strategy to mitigate global warming. Many all-inorganic adsorbents have been studied in this respect. Lately, metal-organic frameworks [1] (MOFs) have emerged as a promising alternative to inorganic materials in gas adsorption. We have recently studied the structural features underneath the remarkable CO2 adsorption capacity (40.5 wt % at 298 K and 10 bar) of $Fe_2(BPEB)_3$ [2] (H₂BPEB = 1,4-bis(1H-pyrazol-4-ylethynyl)benzene), by coupling advanced experimental and computational tools [3]. In situ and operando high-resolution and high-energy PXRD experiments were run at the beamline ID22 of ESRF at 273 and 298 K, dosing CO₂ in the pressure range of 0-20 bar. Juxtaposing structure determination to total scattering analysis enabled us to disclose the CO₂ primary adsorption sites, and the host-guest and guest-guest interactions at all the investigated pressures. Molecular dynamics simulations confirmed the experimentally individuated adsorption sites and helped in characterizing the energetics of the process. Our molecular-level insight into the adsorption of CO₂ by Fe₂(BPEB)₃, a rigid host without exposed metal sites or functional groups with particular affinity to CO₂ on the ligand, affords important information on a debated topic, i.e.: the chemical and structural properties a host should possess for efficient CO2 adsorption under rather mild conditions.

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Keywords: High-resolution PXRD, high-energy PXRD, CO₂ adsorption

MS35-04

Coordination Polymers with Supramolecules as Nodes

Eugenia Peresypkina¹, Dr. Alexander Virovets¹, Prof. Dr. Manfred Scheer²

- 1. Lst. Prof. Dr. M. Scheer, University of Regensburg, Regensburg, Germany
- 2. Dept. of Chemistry and Pharmacy, University of Regensburg, Regensburg, Germany

email: peresyp@niic.nsc.ru

Since 2003, we have been investigating the use of pentaphosphaferrocene [Cp^{*}Fe($\eta^{-}P_{5}$]] (Cp^{*} = η^{5} -C₅R₅, R = Me, CH₂Ph, PhC₄H₉) as a building block in supramolecular chemistry. The phosphorus atoms of the planar P₅-rings are able to coordinate to Cu⁺ and Ag⁺ (M⁺) cations resulting in either coordination polymers with M_x(halogen)_y fragments as nodes or in self-assembled spherical hollow supramolecules of 2.1–4.6 nm in diameter [1-3]. Both coordination polymers and supramolecules can serve as matrices or molecular containers for various small molecules. For example, we succeeded in the encapsulation of metallocenes such as Cp₂Co⁺ [2] (Fig.1a) as well as of metastable molecules such as the tetrahedral molecules white phosphorus, P₄, and yellow arsenic, As₄ [3] (Fig.1b).

A new direction of our research is to connect giant supramolecules by organic linkers to form coordination polymers with entire supramolecules as nodes. Thus, the coordination of Ag⁺ cations to the P₅-rings results in the in situ formation of supramolecules, while the additional coordination of Ag⁺ to N-donor atoms of N≡C(CH₂)_nC≡N (Lⁿ, n=5-10) (Lⁿ) flexible linker, in turn, leads to 1D, 2D and 3D coordination polymers in one-pot reactions. Depending on the experimental conditions, coordination polymers with mononuclear Ag+ nodes can also be obtained. The composition and structure of the supramolecules as well as the dimensionality of the polymer can be controlled by changing the reaction stoichiometry or by adding guest molecules as P_4 . Thus, in the presence of P_4 , two new 1D-polymers were obtained, (P4)@[(Cp*FeP5)9Ag8(L10)4] $(SbF_6)_9$ (Fig.1c) and $[(Cp*FeP_5)_2Ag_2(\mu,\eta^2-P_4)(SbF_6)]SbF_6$ (Fig.1d). The former contains polynuclear cationic nodes of $[Ag_9(Cp*FeP_5)_9]^{9+}$ that encapsulates tetrahedral P₄ molecules in the central cavity.

Effective collaboration between chemists and crystallographers allowed developing effective crystallization methods, skilled crystal handling and proper single-crystal X-ray data collection techniques to perform structural studies at atomic resolution. As a result, fine details of structures containing hundreds of heavy atoms could be analysed, shedding light on the nature of host-guest interactions. In addition to the usual methodological problems as for instance severe crystallographic disorder, the structural studies are occasionally encumbered by the appearance of modulated or incommensurate structures. Financial support from the ERC grant ADG 339072 is gratefully acknowledged. Parts of these investigations were carried out at PETRA III synchrotron source at DESY, a member of the Helmholtz Association (HGF). Fig. 1. *a*) encapsulation of Cp₂Co⁺ in the supramolecule; inclusion of E₄ (E=As, P) molecule into *b*) coordination polymer and *c*) into $[Ag_9(Cp^*FeP_5)_9]^{9^+}$ cage. *d*) $[(Cp^*FeP_5)_2Ag_2(\mu,\eta^2-P_4)(SbF_6)]SbF_6.$



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Keywords: coordination polymer, host-guest compounds, pentaphosphaferrocene

MS35-05

A hierarchical metal-organic framework with breathing-dependent redox activity

Guillermo Minguez Espallargas¹, Manuel Souto¹

1. Instituto de Ciencia Molecular (ICMol), University of Valencia, Valencia, Spain

email: guillermo.minguez@uv.es

Metal-Organic Frameworks (MOFs) combining both large pores and high stability have received a lot of attention during the past years due to their high interest towards practical applications such as MIL-100 or MIL-101. Moreover, the preparation of hierarchical MOFs, presenting both micro- and mesopores, has also become a subject of great interest since micropores contribute to the bulk of the surface area whereas mesopores provide a better accesability to larger molecules to quickly diffuse, becoming very attractive for catalytic applications.[1] Herein we report the synthesis, structure determination and physical properties of MUV-2 (MUV: Materials of University of Valencia), a highly stable tetrathiafulvalene (TTF)-based MOF with a non-interpenetrated hierarchical crystal structure with mesoporous channels (~33 Å) disposed orthogonal to microporous channels (~10 Å). The advantages of MUV-2 respect to widely used MOFs catalyst (MIL-100 and MIL-101) will be clearly demonstrated for a reaction of large applied interest (aerobic oxidation of benzothiophenes), illustrating the advantages of having a hierarchical MOF with large mesopores and high stability.[2] In addition, MUV-2 presents a continuous breathing behaviour upon solvent or gas adsorption, cause by the flexibility of the TTF-based ligands that show conformational changes, as unequivocally demonstrated by single crystal X-ray diffraction. The reversible swelling not only modifies the accessible space, but also the oxidation potential of the MOF.[3]



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Keywords: Highly-stable MOFs, breathing MOFs, hierarchical MOFs



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Keywords: tautomer, metal coordination, salt

MS36-O2

Unexpected structural properties of Ln(III)-complexes formed with the heptadentate AAZTA ligand

Zsolt Baranyai¹, Silvio Aime², Alessandro Maiocchi³, Fulvio Uggeri³, Norberto Masciocchi⁴, Giovanni Battista Giovenzana⁴

- 1. Bracco Research Centre, Basovizza (Trieste), Italy
- Department of Molecular Biotechnologies and Health Sciences, Molecular Imaging Center, University of Torino, Torino, Italy
- Bracco Research Centre, Bracco Imaging spa, Colleretto Giacosa (TO), Italy
- ipartimento di Scienza e Alta Tecnologia and To.Sca.Lab, Università degli Studi dell'Insubria, Como, Italy

email: zsolt.baranyai@bracco.com

The rich variety of magnetic, optical and radiochemical properties of lanthanide(III)-ions (Ln3+) is the reason of the large number of applications of Ln(III)-complexes in several areas of chemistry, biology, medicine and materialscience. In vivo applications requires very robust Ln(III)-complexes characterized by high thermodynamic and kinetic stability in order to limit the competition reactions with endogenous species. AAZTA (Scheme 1) is a mesocyclic chelating agent. Coordination properties of AAZTA towards a wide array of metal ions indicates its remarkable affinities for Ln(III)-ions.1 Even if the Ln(III)ions are very similar, detailed physico-chemical characterizations reveal that the thermodynamic and the kinetic properties, the exchange rate and mechanism of the inner sphere water molecue/s of [Ln(AAZTA)] complexes formed with smaller and larger Ln(III)-ions differ considerably.1,2 To explore the origin of the different physico-chemical properties of [Ln(AAZTA)] complexes, the structural properties of [Nd(AAZTA)], [Er(AAZTA], [Lu(AAZTA)] and [Sc(AAZTA)] were determined by single crystal X-ray diffraction analysis. Crystals of [Ln(AAZTA)] complexes were obtained from a mixture of water and ethanol in the presence of guanidinium, K⁺ and/or NH₄⁺ counter ions. Crystals of [Nd(AAZTA)] (Scheme 1) are characterized by the presence of dimers. Three carboxylate groups behave as monodentate, while the fourth bridges the adjacent centrosymetrically related Nd(III) ion, where one of the two oxygen atoms is shared between the two Nd(III)-ions. The coordination geometry in [Nd(AAZTA)(H2O)] is a distorted bicapped square antiprism with the capping positions occupied by a N atom and one O atom of the bridging carboxylates. One plane of the antiprism is formed by three carboxylate O and the water O atoms, and the other by two N and two carboxylate O atoms. In the [Lu(AAZTA)] complex, the Lu(III) ion is directly bound to seven donor atoms of the AAZTA ligand, octa-coordination being completed by the water O atom in the capping position. The coordination polyhedron of Lu(III) in [Lu(AAZTA)(H₂O)]⁻ can be described by an irregular dodecahedron defined by a 1:4:3 stack of water O atom and of two nearly parallel planes formed by four carboxylate O and three N atoms. This coordination geometry (of idealized C_s symmetry) is unusual and it was not reported in the thorough stereochemical analysis proposed for ideal 8-vertex polyhedra, where 11 different cases were considered.3 By taking into account the structural properties of [Nd(AAZTA)(H₂O)] and [Ln(AAZTA) (H₂O)], the different physico-chemical properties might

be explained by the different coordination geometry of [Ln(AAZTA)] complexes formed by the smaller and larger Ln(III)-ions.



Scheme I, Structures of H₄AAZTA ligand, K₄[Nd(AAZTA)(EO0)]₂ and K[Lu(AAZTA)(H₂O0] complexes

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Keywords: lanthanides, square antiprism, dodecahedron

MS36-O3

Mixed ligand Ni Werner complexes: enhanced selectivity and hydrogen bonding frameworks

Merrill Wicht1, Nikoletta Bathori1, Luigi Nassimbeni1

 Chemistry Department + Cape Peninsula University of Technology, Cape Town, South Africa

email: wichtm@cput.ac.za

A mixed-ligand approach in the synthesis of Werner complexes with central nickel metal and thiocyanate anions with ligands of different aromatic or hydrogen bonding functionalities formed structural intricacy. In the selectivity of xylene isomers, differentiation showed that meta xylene was favoured over the other isomers, ortho xylene (ox), para xylene (px) and ethylbenzene (eb) in the co-ordination with the host Ni(NCS)2(isoquinoline)2(4-phenylpyridine)2.1 The arrangement of the rigid isoquinoline² and the flexible 4-phenylpyridine ligands in trans positions gave the host flexibility to pack meta xylene more intimately than the other isomers. The outcome of the selectivity, mx > eb >ox > px, was confirmed by Hirshfeld surface analysis and void spacing determinations. The 'tunability' of the crystal structures arises from the transformation of the nature and size of the inclusion cavities.3 Attractive functionality using hydrogen bonding of the ligands was reflected in the structure of the complex, Ni(NCS)2(nicotinamide)2(isonicotinamide),. Close packing in the crystal was realised. The complex arrangement of the host showed hydrogen bonding in different directions with amide bonding between the functional groups of the ligands and sulphur of the neighbouring host anion. The use of nickel as the metal centre gives the advantage of geometries not easily accessible in organic structures.

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Keywords: inclusion compound, selectivity, mixed ligand

MS36-O4

Silver(i) complexes as molecularlyengineered lubricants

Luciano Marchio'1, Irene Bassanetti2, Massimiliano Delferro3, Tobin Marks4

- Department of Chemistry, Life Sciences, Environmental Sustainability, Parma, Italy
- 2. Department of Materials Science, University of Milano Bicocca, Milano, Italy
- 3. Argonne National Laboratory, Argonne, United States of America
- Department of Chemistry, Northwestern University, Evanston, United States of America

email: marchio@unipr.it

The use of soft metal deposition for lubrication of sliding materials operating from room to extreme temperature is a field of remarkable interest. Applicative fields are in high speed machinery, advanced heat engine and steel or ceramic industries. Tribological studies of soft metallic layers have been conducted since 1950s and there is a vast literature discussing the use of silver as lubricant material [1]. One of the main problems when using precursors for in silver deposition is the purity of the final layer, since it can be contaminated with P, B, C, and other elements [2, 3]. In this work, we present a series of silver complexes that are able to generate silver layers of high purity. In particular, we considered two classes of nitrogen donor ligands, namely bis-pyrazoles and pyridine-pyrazoles, and two different counterions, NO₂ and BF₄, which are able to yield neutral and ionic complexes, respectively. The TGA profiles of the neutral complexes with the nitrate counter-ion show a sharp single decomposition step in the range 210-260 °C. Powder X-Ray analysis on TGA residues confirmed the presence of pure silver residues. Silver complexes were then deposited on the 52100 stainless steel with the spin-coating technique, and silver layers were produced upon heating at 300 °C. The silver layers were analyzed using powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The silver deposition on the 52100 stainless steel after treatment with Military grade 15W-40 engine oil containing various amounts of silver complexes provided fully flooded lubrication between the pin and disk. We will discuss the structural properties of the complexes that are functional to the silver deposition performances.



Keywords: silver complexes, deposition, anti-wear

MS36-O5

The structure of copper(II)hydroxypiridinecarboxylic acid derivatives in both solid and solution phases

Nóra May¹, Gyula Tamás Gál¹, Valerio B. di Marco², Petra Bombicz¹

- 1. Research Centre for Natural Sciences, Hungarian Academy of Sciences, Budapest, Hungary
- 2. Department of Chemical Sciences, University of Padova, Padova, Italy

email: nagy.nora.veronika@gmail.com

Metal complexes of small biomolecules are frequently used as bioactive compounds in diverse fields of clinical practices. The structure and physico-chemical properties such as solubility and stability of these functional metal complexes are usually fine-tuned in order to optimize the bioavailability and bioactivity. Single crystal X-ray diffraction (SXRD) is one of the most powerful technique for the investigation of the structures of these organic compounds and their complexes in solid phase. However, this method has some weaknesses in case of biologically relevant compounds. Firstly, the preparation of a good quality and suitable size crystal, in many cases, requires sophisticated techniques. Secondly, a number of complexes with different compositions and structures are generally formed in aqueous solution, and so the coexistence of various species is rather typical. This means that the majority of complexes cannot be obtained and studied in crystalline form. Another question is whether the structure of the complex obtained as a single crystal is identical with the one was observed in the solution. These problems warrant the use of another technique in combination with SXRD in which the equilibrium systems of biologically relevant metal complexes can be investigated in solution. In case of paramagnetic metal complexes (such as copper(II)) electron paramagnetic resoncance (EPR) spectroscopy is an extremely sensitive technique to detect the chemical surrounding of the unpaired electron and provides unique local structural information. In the present work we use pH-dependent EPR spectroscopy in combination with SXRD to investigate the complexation properties of a series of substituted hydroxypyridinecarboxylic acids (HPCs)^{1,2} with copper(II). The solution equilibrium system of their copper(II) complexes were investigated by EPR and their bis-ligand [CuL2] complexes were crystallized then investigated by SXRD technique resulted in complementary outcome of the solid and liquid phases.

Acknowledgement

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Keywords: copper(II) complex, electron paramagnetic resonance, solid vs solution

MS37 Mechanochemistry: structure and reaction

Chairs: Dr. Hamish Yeung, Dr. Tomislav Friscic

MS37-01

Is a mechanochemical reaction always truly mechanochemical?

Adam Michalchuk1, Elena Boldyreva2

- Novosibirsk State University, Novosibirsk, Russian Federation and EaStCHEM School of Chemistry, University of Edinburgh, Edinburgh, United Kingdom
- 2. Novosibirsk State University, Novosibirsk, Russia

email: adam.michalchuk@ed.ac.uk

Mechanochemistry has surged in popularity, and is now commonplace in many chemical and materials sciences laboratories. Successful examples of mechanochemical techniques being used in multi-component crystallisation, chemical and bio-chemical synthesis and in the field of supramolecular chemistry are now widely known. However, while many of these examples employ mechanochemical techniques, are they truly mechanochemical in nature? This talk will explore a variety of examples where mechanical energy has been used to induce a chemical or physical change in solid-state systems. A variety of effects that result from the mechanical treatment of solids will be discussed, encompassing both single and multi-phase systems. Particular emphasis will be placed on distinguishing between processes that are directly driven by mechanical energy (e.g. mechanically induced chemical reactions), indirectly driven by mechanical energy (e.g. driven by a product of the mechanical energy), and those that are facilitated by it (e.g. those that would proceed in the absence of mechanical energy).

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Keywords: Mechanochemistry, Solid State Reactions

MS37-O2

New insights in mechanochemical processes using real-time in situ investigations

Franziska Emmerling¹, Irina Akhmetova¹, Hannes Kul¹, Sebastian Haferkamp¹

1. Analytical Chemistry Federal Institute for Materials Research and Testing, Berlin, Germany

email: franziska.emmerling@bam.de

Mechanochemistry is a fast and efficient method applicable for the synthesis of new organic^[1], metal-organic^[2], and inorganic^[3] compounds. The direct monitoring of milling reactions is still challenging. The underlying reaction mechanisms remain often unclear. In the last years, have established a tandem in situ approach for investigating mechanochemical reactions using time-resolved in situ XRD coupled with Raman spectroscopy.^[4] Here, we present an in situ coupling of synchrotron XRD, Raman spectroscopy, and thermography allowing the observation of mechanochemical reactions in real time.^[5] Information on the crystalline, molecular, and temperature state of the materials during grinding could be collected. The chemical composition of the reaction mixture was found to be directly correlated with changes in the temperature profile of the reaction. Furthermore, the presented setup allows the detection of crystalline, amorphous, eutectic as well as liquid intermediates. The resulting deeper kinetic and thermodynamic understanding of milling processes is the key for future optimization of mechanochemical syntheses.



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Maierhofer, C. , Rademann, K., Emmerling, F., Angew. Chem. Int. Ed. 2018, doi:10.1002/anie.201800147.

Keywords: in situ, XRD, Raman spectroscopy

MS37-O3

Milling for better pharmaceuticals: green synthesis, phase transformations and reaction kinetics of vitamin B₃:C cocrystal polymorphs studied in situ

Tomislav Stolar¹, Stipe Lukin¹, Martina Tireli¹, Marco di Michiel², Igor Dejanović³, Ivan Halasz¹, Krunoslav Užarević¹

- 1. Laboratory for Green Synthesis, Division of Physical Chemistry, Ruder Bošković Institute, Zagreb, Croatia
- 2. ESRF European Synchrotron Radiation Facility, Grenoble, France
- Faculty of Chemical Engineering and Technology, University of Zagreb, Zagreb, Croatia

email: tomislav.stolar@irb.hr

The use of mechanochemistry continues to grow due to its efficiency, selectivity and greener way in obtaining desired products. Inability to directly and in real-time monitor reaction progress of milling reactions, without the need to obstruct the milling process, was historically considered as a main drawback of mechanochemistry. This has been recently addressed by advanced synchrotron powder X-ray diffraction¹ and laboratory Raman spectroscopy² in situ monitoring methods which provided a direct insight into physical and chemical changes in reaction mixtures. Utilization of mechanochemistry in pharmaceutical industry is driven primarily by increasing need to create more sustainable drug manufacturing processes. Here we present mechanistic study of mechanochemical cocrystal synthesis of nicotin-amide (vitamin B₁) and L-ascorbic acid (vitamin C).

Using ethanol and methanol as additives in milling 1:1 reaction mixture we have obtained two vitamin B_3 :C cocrystal polymorphs. Kinetically favored polymorph I is known from the literature³ and is in fact intermediate in the formation of previously unknown polymorph II which is thermodynamically more stable. We have successfully solved crystal structure of B_3 :C cocrystal polymorph II from synchrotron powder X-ray diffraction data.

Both polymorphs remained in their respective solid forms even after 6 months of shelf life. Thermodynamic relationship of cocrystal polymorphs was determined by competitive slurry experiment which resulted in pure cocrystal polymorph II. Scaling up manufacturing process for both cocrystal polymorphs up to 10 grams and 100 grams has been achieved using planetary mill and twin screw extruder, respectively. Mechanochemically obtained cocrystal polymorph exhibit excellent tableting properties compared to their reactants. This is important since L-ascorbic acid is famous for having poor compactible properties. Solution cocrystalization experiments resulted always in kinetically favored polymorph I, whereas the thermodynamically more stable polymorph II is available exclusively by mechanochemical milling.

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Keywords: mechanochemistry, pharmaceuticals, in situ

MS37-O4

Crystal adaptronics: mechanically reconfigurable elastic and superelastic molecular crystals

Pance Naumov1, Ejaz Ahmed1, Durga Prasad Karothu1

1. New York University Adbu Dhabi, Abu Dhabi, United Arab Emirates

email: pance.naumov@nyu.edu

Mechanically reconfigurable molecular crystals - ordered materials that can adapt to variable operating and environmental conditions by deformation, whereby they attain motility or perform work - are quickly shaping up a new research direction in materials science, crystal adaptronics. Properties such as elasticity, superelasticity and ferroelasticity that are normally related to inorganic materials, and phenomena such as shape-memory and self-healing effects which are well established for soft materials, are increasingly reported for molecular crystals, yet their mechanism, quantification, and relation to the crystal structure in organic crystals are not immediately intelligible to the chemistry and materials science research communities. This talk will provide a condensed topical overview of the elastic, superelastic and ferroelastic molecular crystals, emerging new classes of materials that bridge the gap between the soft matter and inorganic materials. The occurrence and detection of these unconventional properties, and the underlying structural features of the related molecular materials will be discussed and highlighted together with selected prominent recent examples.

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 Ahmed, E., Karothu, D. P. & Naumov, P. (2018) Angew. Chem. Int. Ed., doi: 10.1002/anie.201800137Keywords: mechanical effects, elasticity, actuators

Keywords: mechanical effects, elasticity, actuators

MS37-O5

Mechanochemistry, a tool for improving drug physicochemical properties and delivery: salt formation and metal coordination

Maria Teresa Duarte¹, Inês C.B. Marins¹, Sílvia Quaresma¹, Vânia André¹

1. Centro de Química Estrutural, Instituto Superior Técnico, Lisboa, Portugal

email: teresa.duarte@tecnico.ulisboa.pt

Mechanochemical strategies were used for solving folic acid solubility issues as well as improving gabapentin polymorphic stability. Biological active Metal Organic Frameworks were synthesized and proved to be promising for drug delivery as the release is achieved through the degradation of the solid. Structures were determined by X-ray powder and single crystal diffraction and SSNMR. MD calculations were used to ascertain experimental results obtained both when controlling the stability of polymorphs as well as attesting SS-NMR results.

This results were obtained in our group when developing strategies to enhance poor aqueous solubility, low dissolution rate and low bioavailability, well known problems of 40% of the approved Active Pharmaceutical Ingredients (APIs) in the market.

Similarly, we have been addressing the use of metal organic frameworks, based on safe metals and drug based linkers to attain controlled delivery. The API is part of the matrix, avoiding multistep procedures to prepare the loaded material, porosity is no longer required.

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Keywords: mechanochemistry, salt formation, metal organic frameworks

MS38 X-Ray diffraction on the micro-s and ps time scale

Chairs: Dr. Gergely Katona, Dr. Ullrich Pietsch

MS38-01

Commissioning experiments at FemtoMAX - An X-ray beamline for structural dynamics

Jörgen Larsson¹, Henrik Enquist², Andrius Jurgilaitis², Amelie Jarnao³, Thai Van Pham², Åsa Bengtsson¹, Carl Ekström¹, Xiaocui Wang¹, David Kroon²

1. Department of Physics, Lund University, Lund, Sweden

2. MAX IV Laboratory, Lund University, Lund, Sweden

3. Synchrotron Soleil, Paris, France

email: jorgen.larsson@fysik.lth.se

The FemtoMAX beamline [1] is driven by the linear accelerator (LINAC) at MAX IV. The design of the LIN-AC allows for electron bunches shorter than 100 fs in duration. We will, describe the FemtoMAX beamline and show some of the early commissioning experiments. The MAX IV LINAC is operated at 3 GeV energy and 2 Hz repetition rate. An upgrade to 100 Hz is mainly limited by a lack of a radiation safety permit for higher repetition rates. The electron bunches have a duration of 100 fs for a bunch charge of 100 pC. The MAX IV LINAC is a stable electron source, as the pulse charge vary less than 10%, and the fluctuations of position and angle of the beam fall within 10% of the beam size and divergence. The Femto-MAX beamline is equipped with a 666 period undulator with 10 m active length. When the short electron pulses are sent through this insertion device they emit femtosecond X-ray pulses with photon energy from 1.8 keV and higher. We will describe the X-ray optics including focusing optics, monochromator options and X-ray beam position monitors. An ultrafast laser system provides femtosecond optical pulses for optical pump - X-ray probe experiments. The laser system is located in a laser laboratory directly above the beamline. The laser oscillator is synchronized to the 3 GHz RF signal originating from the master oscillator. The synchronization between laser and electrons are monitored by an optical cross-correlator and a RF filter-based jitter-monitor. The direct timing of the laser relative to X-rays can be measured by a UV-sensitive, X-ray streak camera. End stations for scattering and spectroscopy are built to be interchangeable, whereas a chamber for atomic and molecular physics is placed behind the scattering and spectroscopy end-station. We will present the first experiments demonstrating the beamline capabilities. These experiments include strain generated in an optoacoustic transducer [2] and non-thermal melting.

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 FemtoMAX - an X-ray beamline for structural dynamics at the shortpulse facility of MAX IV Journal of Synchrotron Radiation 25, 570 (2018) https://doi. org/10.1107/S1600577517017660
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Demonstration of a 20 ps X-ray switch based on a photoacoustic transducer

Structural Dynamics 4, 051102 (2017) http://aca.scitation. org/doi/10.1063/1.4993730

Keywords: Time-resolved Diffraction, Beamline, Non-thermal melting



Serial Crystallography - Exciting possibilities for time resolved Structural Biology

Dominik Oberthuer

 Center for Free-Electron Laser Science - Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany

email: dominik.oberthuer@desy.de

An overview will be given on recent developments in XFEL- and synchrotron based serial crystallography towards time-resolved structural biology. Methods will be presented and discussed, as well as limitations and future prospects.

Keywords: Serial Crystallography, Time Resolved Crystallography, Structural Biology

MS38-O3

Short and long-term structural effects of terahertz radiation on cryo-cooled bovine trypsin crystals

Viktor Ahlberg Gagnér¹, Ida Lundholm¹, Maria-José Garcia Bonete¹, Helena Rodilla², Vitali Zhaunerchyk³, Gleb Bourenkov⁴, Thomas Schneider⁴, Jan Starke⁵, Gergely Katona¹

- The Department of Chememistry and Molecular Biology, The University of Gothenburg, Gothenburg, Sweden
- Terahertz and Millimetre Wave Laboratory, Chalmers University of Technology, Gothenburg, Sweden
- Department of Physics, The University of Gothenburg, Gothenburg, Sweden
- 4. EMBL Hamburg c/o DESY, Hamburg, Germany
- 5. Terahertz and Millimetre Wave Laboratory, Chalmers University of Technology, Gothenburg, Sweden

email: viktor.ahlberg.gagner@gu.se

The use of non-ionizing Terahertz (THz) radiation in technology is a new growing field. New methods utilise THz radiation in for instance security screening at airports and border controls, and in medical diagnostics [1]. In contrast to x-rays, the THz radiation can non-destructively screen medical patients. In addition, the radiation generates a high contrast in soft tissue due to water absorption, and has higher spatial resolution compared to MRI and ultrasound [2]. Albeit non-ionizing, research have shown that THz radiation might still induce changes biomolecules due to collective oscillations [3]. In addition, a report from the U.S. National Toxicology Program states that non-ionizing radio waves from cell phones might have a cancerous effect. Therefore, it is imperative to study this protein-radiation interaction, not only for the sake of potential adverse effects biological systems, but also for the new insight this information provide to protein - light interactions.

To research the effect of THz interactions, bovine trypsin was crystallized, flash-cooled to 100 K, and studied in a pump-probe x-ray crystallography experiment. During the experiment, the crystals were pumped with 0.5 THz radiation, for 22.5 ms, and simultaneously probed with 14 KeV x-rays during 25 ms, with no THz radiation at half of the duty cycle. The data (diffraction up to 1.15 Å) show differences in the isotropic and anisotropic contribution of the atomic displacement parameter (ADP) tensor, for individual atoms. The differences are detected during both short term timescales (differences between odd and even frames), and long term timescales (differences between THz-radiated and reference crystals). Additionally, the ADP tensor forms functional links to seemingly unrelated parts of the protein. In general, these data indicate a structural order which is induced by the THz radiation, in contrast to the general disorder, expected from an increased thermal energy.

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Keywords: Crystallography, THz radiation

MS38-O4

Time-resolved crystallography via an interlacing approach allows elucidation of milliseconds to seconds time delays

Pedram Mehrabi¹, Eike Schulz¹, Henrike M. Müller-Werkmeister², Elke Persch³, Raoul De Gasparo³, Francois Diederich³, Friedjof Tellkamp⁴, Emil Pai⁵, R.J. Dwayne Miller¹

- 1. Atomically Resolved Dynamics Department | Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany)
- 2. Institute of Chemistry, Physical Chemistry | University of Potsdam, Postdam, Germany
- 3. Laboratorium für Organische Chemie | ETH Zürich, Zürich, Switzerland
- Scientific Support Unit Machine Physics | Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany
- 5. Department of Biochemistry | University of Toronto, Toronto, Canada

email: pedram.mehrabi@mpsd.mpg.de

Time-resolved crystallography has recently seen a resurgence with the advent of very bright X-ray sources. However, time-resolved studies of enzymatic systems is often hindered by difficulties of acquiring time points which span the entire reaction coordinate pathway. Using a model system, fluoroacetate dehalogenase, to examine chemically triggered reactions, a proof-of-principle method using a chip as a fixed target, as well as a novel "interlacing" approach to data acquisition, timepoints ranging from milliseconds to several seconds can be acquired. Enabling >100k images to be collected within a few hours. Due to most enzymes not being susceptible to photoinduction, using caged fluoroacetate (2(4-hydroxyphenyl)-2-oxoethyl fluoroacetate), reaction initiation was achieved by photolytic cleavage via a femtosecond laser pulse of. Data collection was performed at both the P11 and P14 beamlines at the PETRA III synchrotron on sub-25-micron crystals. Multiple time points were collected spanning a range from milliseconds to several seconds producing well-resolved electron density maps ranging from 1.75-2 Å in resolution. Preliminary results showed significant structural changes in both the active site as well as dynamic changes in the cap domain, which support previously published results obtained by mutant trapping [1]. This newly developed method is highly flexible and can be used on numerous different enzymatic systems and can be adapted for use at XFELs as well as synchrotrons with bright microfocus beamlines.

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 Kim, T.H. et al. (2017). The role of dimer asymmetry and protomer dynamics in enzyme catalysis. Science. 355(6322): eaag2355. Keywords: Time-resolved crystallography, crystallography, enzymology, method development

Keywords: Time-resolved crystallography, crystallography, enzymology, method development

MS38-O5

Ultrafast three dimensional X-ray imaging of strain dynamics in pulse-heated nanocrystals

Kiran Sasikumar¹, Mathew Cherukara², Thomas Peterka³, Ross Harder², Subramanian Sankaranarayanan⁴

- 1. Avant-garde Materials Simulation Deutschland GmbH, Freiburg, Germany
- 2. X-ray Sciences Division, Argonne National Laboratory, Lemont, United States of America
- 3. Mathematics and Computer Science, Argonne National Laboratory, Lemont, United States of America
- Center for Nanoscale Materials, Argonne National Laboratory, Lemont, United States of America

email: kirans1987@gmail.com

The use of nanomaterials have become ubiquitous in several technological applications such as heat dissipation in semiconductors, thermal therapeutics via intensely heated nanofluids, and waste heat energy conversion via thermoelectric materials. Understanding the energy transport via lattice vibrations, under non-equilibrium conditions, play an integral role in the further maturing of these technologies. Three-dimensional imaging of the dynamical response of nanomaterials following ultrafast excitation can reveal energy transduction mechanisms, their dissipation pathways, as well as provide insight into material stability under conditions far from equilibrium.

Such dynamical behavior is extremely challenging to characterize especially at nano- to picosecond timescales. Recent advances in experimental techniques at x-ray synchrotron sources have enabled time-dependent measurements of three-dimensional strain evolution in nanomaterials. In particular, excitation by an ultrafast laser 'pump' and Bragg Coherent Diffraction Imaging (BCDI) using stroboscopic probes' of X-rays have been used to directly image lattice distortions within nanocrystals. Furthermore, with advances in high-performance computing and the use of machine learning approaches in material science, modeling and in-situ data analysis that complement BCDI measurements have provided crucial insights for energy research. Here, we provide a short review of recent progress in the integrated imaging (BCDI) and simulation (continuum and/or atomistic) approach that has been employed to characterize ultrafast lattice distortions on a wide class of material systems.

First, we discuss the laser pump excitation of zinc oxide nanocrystals to directly image the propagation of acoustic phonons at nanosecond timescales. By directly importing the experimentally reconstructed nanocrystal structure into a continuum deformation model, we identify the characteristic resonant modes excited by the laser pulse and characterize the electric potential gradients induced across the piezoelectric nanocrystal. Second, we characterize the deformation modes of core/shell semiconductor/metal nanorods following pulse-laser excitation of the metallic shell. An experimentally informed thermo-electromechanical continuum model elucidates the origin of the deformation modes observed experimentally. Third, we demonstrate inhomogeneous effects in lattice breathing at picosecond timescales, following femtosecond-pulse laser heating of bimetal core-shell nanocrystals, using multi-million-atom

molecular dynamics simulations that directly complement BCDI images.

Overall, we show how a coupled imaging and simulation approach enables visualizing the dynamical response of material heterointerfaces, with implications for the design of tailored functional devices.

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Keywords: Diffraction, phonons, simulation

MS39 The use of X-rays and neutrons for experiments in nanoscience

Chairs: Dr. Rainer Timm, Prof. Jordi Arbiol

MS39-01

Correlative cryo soft X-ray imaging of cells

Eva Pereiro¹, Ana J. Pérez-Berná¹, Andrea Sorrentino¹, Pablo Gastaminza², Neta Varsano³, Lia Addadi³, Sergey Kapishnikov⁴, Jens Als-Nielsen⁴

- 1. Experiments Division, Alba Synchrotron Light Source, Barcelona, Spain
- 2. Department of Molecular and Cellular Biology, CNB-CSIC, Madrid, Spain
- Department of Structural Biology, Weizmann Institute of Science, Rehovot, Israel
- Niels Bohr Institute, University of Copenhagen, Copenhagen, Denmark

email: epereiro@cells.es

Cryo soft X-ray tomography of whole cells in the water window energy range can provide relevant structural information of complex cellular phenomena with chemical sensitivity at spatial resolutions of 30 nm. Functional studies are achieved by correlating this information with visible light fluorescence on the same cell, but also by combining electron microscopy or even cryo X-ray fluorescence. Examples of correlative studies will be presented. First, we will focus on the structural changes in Hepatitis C infected cells [1]; second, on cholesterol crystal early formation in cells combining STORM [2] and finally on the heme detoxification process in the malaria parasite [3].

Keywords: X-ray imaging, correlative microscopy, cryo

MS39-O2

Complete structure analysis of single cores shell nanowires by X-ray methods

Ullrich Pietsch¹, Ali Al Hassan², Arman Davtyan², Hanno Küpers³, Lutz Geelhaar³

- 1. Physics, Siegen, Germany
- 2. University of Siegen, Siegen, Germany
- 3. Paul Drude Institute, Berlin, Germany

email: pietsch@physik.uni-siegen.de

It is known that core-shell-shell semiconductor nanowires (NW) grow pseudomorph along the growth direction, i.e. the axial lattice parameters of core and shell materials are the same. Therefore, both structural composition and interface strain of the NW are encoded along directions perpendicular to the growth axis. In this work, we determine the complete structure of single GaAs/(In,Ga)As/GaAs core-shell-shell NW heterostructres with core diameter of 50 nm and (In,Ga) As shell thickness of 20 nm with nominal indium concentration of 15% capped by 30 nm GaAs outer shell MBE grown on prepatterned silicon (111) substrates by means of x-ray nano-diffraction using synchrotron radiation. In order to access single NWs by x-ray nano beam being incident parallel to the surface of the substrate, a single row of holes with seperation of 10 µm was defined by electron beam lithography to act as nucleation centers for MBE NW growth. These well separated NWs were probed sequencially by X-ray nano diffraction recording 3D reciprocal space maps (RSM) of Bragg reflections with scattering vectors parallel (out-of-plane) and perpendicular (in-plane) to the NW growth axis. From the out-of-plane (111) Bragg reflection, we derived deviations from the hexagonal symmetry and diameters of the probed NWs grown under the same conditions. The radial NW composition and interface strain became accessible measuring the 2D scattering intensity distributions of the in-plane (2-20) and (22-4) reflections exhibiting well pronounced thickness oscillations perpendicular to the NW side planes (truncation rods - TR). Quantitative values of thickness, composition and strain acting at the (In,Ga)As and GaAs shells were obtained via finite element modelling (FEM) of the core-shell-shell NW and subsequent Fourier transformation simulating the TRs measured along the three different directions of the hexagonally shaped NWs simultaneously. Considering the experimental constraints of the current experiment, thicknesses and In content have been evaluated with uncertainty of ± 2 nm and \pm 0.01%, respectively. Comparing data taken from different single NWs, the shells thicknesses differ between one and the other.

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Keywords: Semiconductor nanowires, X-ray nanodiffraction

MS39-O3

Novel usage of neutron scattering: holography for observations of local atomic structures of light elements

Kenji Ohoyama¹, Yohei Fukumoto¹, Shoichi Uechi¹, Yuki Kanazawa¹, Kouichi Hayashi², Naohisa Happo¹, Masahide Harada³, Yasuhiro Inamura³, Kenichi Oikawa³

- Graduate School of Science and Engineering, Ibaraki University, Tokai, Japan
- Frontier Research Institute for Materials Research, Nagoya Institute of Technology, Nagoya, Japan
- 3. J-PARC Center, Japan Atomic Energy Agency, Tokai, Japan

email: kenji.ohoyama.vs@vc.ibaraki.ac.jp

As a new view point of structural physics, understanding of three-dimensional (3D) local atomic structures, such as slight changes of atomic structures around dopants in functional materials, or local lattice distortions in mixed crystals, must generate breakthroughs in novel materials science Atomic resolution holography (ARH) is a quite unique and indispensable probe for local atomic structure investigations, because it has following important advantages: (a) 3D local structures without translation symmetry can be directly observed without models (b) Observable range is \sim 20 Å, which is much longer than lattice constants of most inorganic materials. (c) The central atom can be selected In particular, neutron ARH is the best probe to visualise local structures of materials which include light elements, such as H, B, or O.

Neutron holography was firstly proposed by Cser et al.[1], and was demonstrated using a single crystal of Al-₄Ta₃O₁₃(OH) by Sur *et al.* in a reactor facility in 2001[2]. The authors also succeeded in neutron holography in a reactor facility in Japan in 2008. However, in reactor facilities, holograms with only one wavelength could be obtained; accuracy of obtained atomic images by such single-wavelength ARH measurements is insufficient because of many ghost images or artifacts. To avoid these, multi-wavelength ARH, which uses many holograms with different wavelengths, is quite effective for reconstructions of accurate atomic images. Thus, the authors have developed white neutron ARH in the pulsed neutron facility, Japan Proton Accelerator Research Complex (J-PARC) at Tokai, Japan because one can obtain over 100 holograms with different wavelengths by time-of-flight method, and succeeded in visualising local atomic structures around Eu in 1 % Eu doped CaF₂, which is a typical scintillation crystal, and have found that local distortion of Ca and excess F around Eu[3].

By the development of the white neutron ARH, the authors have also succeeded in visualising clear images of local atomic structures around dopants in many materials, such as B doped Si, Sm doped RB₆ (R=Yb, La) already. These recent results indicate that white neutron ARH will be an indispensable probe for structural circumstances of various materials with light elements, for instance, hydrides or B doped functional materials. In our presentation, recent results of white neutron ARH will be reported as well as its brief principle and advantages.
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Keywords: Neutron holography, Local atomic structure, Doped functional materials

MS39-O4

Analysis of short range phenomena in novel materials using the PDF-method

Philipp Hans1, Reinhard B. Neder2, Klaudia Hradil1

- 1 .X-ray center TU Wien, Vienna, Austria
- Crystallography and structural physics Friedrich-Alexander Universität Erlangen-Nürnberg, Erlangen, Germany

email: philipp.hans@tuwien.ac.at

In the present contribution, we will show results and further progress in analysis of pair distribution function (PDF) studies on amorphous materials containing crystalline domains. The materials are of stoichiometry (SiO₂)_x(TiO₂)_y. The synthesizers' ([1]) aim was to prepare a material that is similar to the zeolithe TS-1 (titanium silicalite), which exhibits catalytic properties (eg phenol hydroxylation) but is amorphous and thus mechanical more stable. - The focus of this work is not on catalytical activity but on structural features.

A big research question concerns the coordination number of the Ti-atoms with respect to oxygen. Extensive studies (Rietveld analyses and neutron scattering using isotope substitution) have been done on TS-1 (see [2]). Literature states that 4-fold coordination is necessary for the material to exhibit catalytic properties and that incorporation of Ti-atoms into the bulk-SiO₂, thereby substituting Si, happens only at low Ti-contents ([3]). The origin of catalytic properties of TS-1 is still an open topic and no consesus has been reached in literature.

The experimental PDF could be modelled with a contribution by amorphous SiO₂ and small spherically shaped crystalline TiO₂-particles in the Rutile modification, i.e. Ti in six-fold coordination. A model based on a pure glass phase with Si partially substituted by Ti in four fold coodinatikon did not result in as good an agreement. The features in the difference PDF indicate interaction between the particles and the surrounding matrix. TEM and SAXS measurements indicate a structure of elongated pores, but due to electrostatic charging in the TEM no magnification sufficient for the detection of the small TiO₂ particles could be achieved.

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Keywords: pair distribution function, amorphous, catalysis

MS39-O5

The argentinean neutron beams laboratory project

Gabriela Aurelio¹, Javier Santisteban², Karina Pierpauli², Florencia Cantargi², Miguel Ángel Vicente², Aureliano Tartaglione²

- 1. Centro Atómico Bariloche, San Carlos de Bariloche, Argentina
- Centro Atómico Bariloche, Comisión Nacional de Energía Atómica, S. C. de Bariloche, Argentina

email: gaurelio@cab.cnea.gov.ar

The RA-10 is a 30 MW multi-purpose reactor under construction in Buenos Aires, designed to satisfy national and regional demand for radioisotopes, nuclear materials testing and neutron beams research. The reactor will start operations on 2021, it will have a liquid deuterium cold source and a large guide hall for instruments.

Since 2016 the National Atomic Energy Commission has started a project called "The Argentinean neutron beams laboratory for the RA-10 reactor" (LAHN); aimed at implementing state-of-the-art instruments, developing a user community and the laboratory staff. Two instruments are being designed for the first stage of this laboratory:

(i) a neutron imaging instrument on a cold beam; and (ii) a multi-purpose diffractometer on a thermal beam, optimized for non-destructive studies on large objects.

Both instruments will be placed on the reactor face, in order to exploit very intense, undisturbed, neutron beams. Besides this, an ambitious program has started to popularize neutron techniques in Argentina and create new users. A second phase for the project has been launched, taking into consideration the demands of the local and regional scientific community. Several instruments are being evaluated for this second phase in view of the proposals we have received from laboratories in Europe.

In this talk, the present state of the project will described, providing details of the instruments design and the strategies implemented to develop the Argentinean users community.

Keywords: large-scale facilities, neutron diffractometer, research reactor

MS40 Crystallization for small and large molecules

Chairs: Prof. Bernhard Spingler, Prof. Terese Bergfors

MS40-01

Revisiting polymorphism of molecular crystals from the melt

Alexander Shtukenberg1, Qiang Zhu2, Bart Kahr1

- 1. Department of Chemistry, New York University, New York, United States of America
- Department of Physics and Astronomy, High Pressure Science and Engineering Center, University of Nevada Las Vegas, Las Vegas, United States of America

email: shtukenberg@mail.ru

Polymorphism is a typical feature of molecular crystals. Since polymorphic modifications exhibit different physical properties, polymorph screening has become an important part of drug formulation process and is required for other applications of molecular crystals. Despite being not as universal as solution screening, melt crystallization typically combines high driving forces for crystallization with low nucleation and growth rates and can provide polymorphs not accessible in a standard solution screening. The screening process itself is simple, fast, and cheap, while determination of the crystal structures is often complicated by the absence of crystals suitable for the single crystal X-ray diffraction analysis. Nevertheless, advances in powder X-ray diffraction and crystal structure prediction algorithms, today, can fill the breach in order to extract structure from polycrystalline samples. Various organic compounds were crystallized from the melt and observed with a polarized light optical microscope. Polymorphs distinguished optically were further analyzed using Raman spectroscopy and X-ray powder diffraction. The crystal structures were typically solved using a combination of X-ray powder diffraction, crystal structure prediction, and Rietveld refinement. We illustrate this approach by discovering and characterizing new polymorphs of several common and well-studied compounds including resorcinol, coumarin, aspirin, and benzamide.

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Keywords: polymorphism, molecular crystals, melt crystallization

MS40-O2

The good, the bad and the ugly: small and macro molecular crystals in all their glory

Elspeth Garman1

1. Department of Biochemistry, University of Oxford, Oxford, United Kingdom

email: elspeth.garman@bioch.ox.ac.uk

Both small and macromolecular crystals can be beautiful objects that are a joy to behold, both in real and reciprocal space. However, sometimes they can look optically perfect but give very disappointing (or no) diffraction or *vice versa*, and their behaviour in this regard is somewhat unpredictable [1]. Nonetheless, given a good, bad or ugly crystal, we can optimise the outcome of diffraction experiments by thinking about the conditions to which we subject the sample from the point of view of the crystal. This talk will expand upon the above theme, and use a cacophony of examples collected over 30 years of working in crystallography, ending with a particularly tricky one to illustrate the challenges that are sometimes faced in macromolecular structure determination by crystallography [2].

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Keywords: crystals, diffraction, challenges

MS40-O3

Novel screening method for the crystallization of salts of organic cations

Martin Babor¹, Philipp Nievergel², Jan Čejka¹, Bernhard Spingler²

- Department of Solid State Chemistry, University of Chemistry and Technology in Prague, Prague, Czech Republic
- Department of Chemistry, University of Zurich, Zurich, Switzerland

email: Baborm@vscht.cz

Charged organic cations are an important part of chemical and especially pharmaceutical industry. Over 38% of all solid active pharmaceutical ingredients (APIs) are used in form of the cation with some suitable anion. Nowadays, there is a trend to use counterions other than the very popular chloride. [1] Different salts of the same API provide different physicochemical properties as solubility depending on pH, stability, hygroscopicity and so on. Traditional salt screenings are time, material and labor work consuming. We present a new modification of the small-scale vapor diffusion crystallization technique of macromolecules with the purpose of anion screening for an organic cation. The basic ideas of our screening are an ion exchange and crystallization using vapor diffusion. This crystallization leads in most cases to high-quality single crystals measurable on an in-house X-ray diffractometer. The screening itself was performed with 7 structurally significantly different compounds, whose aqueous solubilities vary by a factor of almost 1000. The screening was highly effective. At least one new salt was found for 6 out of 7 compounds. To summarize the screening. 18 new salts were found and structurally described. We are able to prepare about 550 crystallization experiments per hour. And the screening of 96 conditions consumes only between 26 µg - 22 mg of a substance depending on their solubility. [2]



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Keywords: Salts screening, Pharmaceuticals, X-ray diffraction

MS40-O4

Crystallophore, a unique nucleating and phasing agent for biocrystallography

Eric Girard¹, Sylvain Engilberge¹, Tristan Wagner², François Riobé³, Olivier Maury³

- 1. Institut de Biologie Structurale, GRENOBLE, France
- Max Planck Institute for Terrestrial Microbiology, MARBURG, Germany
- 3. École Normale Supérieure, LYON, France

email: eric.girard@ibs.fr

With 90% of the structures present in Protein Data Bank, crystallography is one of the methods of choice for obtaining structural information on proteins. However, the method still suffers from the two inherent locks: obtaining single crystals and solving the phase problem. The crystallization of proteins thus remains the major lock and we consider that approximately one purified protein out of three will lead to exploitable crystals and this, in spite of the exploration of hundreds of physico-chemical conditions allowed by the crystallization robots and the development of numerous crystallization kits. Another approach is the use of nucleating agents (heterogeneous nucleation) to lower the energy required to form the crystalline germ such as Molecular Imprinted Polymers (Saridakis & Chayen, 2013).

We recently proposed a new molecule, called Crystallophore (Xo4), which acts as a nucleating agent (Engilberge *et al.*, 2017). Xo4 is a lanthanide complex formed from a molecular cage chelating a lanthanide atom. We will present the results obtained on about fifteen proteins which show that Xo4 induces unique crystallization conditions (Figure 1a) and promotes new crystal packing thanks to supramolecular interactions.

The lanthanide atom present in Xo4 also makes it possible to obtain an important anomalous signal that greatly facilitates the phase determination process, as illustrated by various examples (Engilberge *et al.*, 2017; Vögeli *et al.*, 2018) (Figure 1b).

The versatility of the interactions between Xo4 and the surface of proteins explains its exceptional properties making this molecule a unique tool for simultaneously solving the two major locks of biocrystallography.

Figure 1: a) Examples of crystallization drops obtained without (top) and with Xo4 (bottom) for three different proteins. b) Structure of the complex thiolase/HMGCS/ DUF35 involved in the synthesis of mevalonate (Vögeli *et al.*, 2018).



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Keywords: Protein crystallization, structure determination, crystallophore

MS40-O5

Current challenges of obtaining crystals for bio-crystallography

Monika Spano¹, Niels Junius¹, Elham Vahdatahar¹, Sofia Jaho¹, Christophe Berzin², Yoann Sallaz-Damaz³, David Cobessi³, Jean-Luc Ferrer²

- 1. Université Grenoble Alpes, Institut de Biologie Structurale, Grenoble, France
- 2. CEA, Institut de Biologie Structurale, Grenoble, France
- 3. CNRS, Institut de Biologie Structurale, Grenoble, France

email: monika.spano@ibs.fr

A rational way to find the proper conditions to grow crystal samples for Bio-Crystallography is to determine the crystallization phase diagram, which allows a punctual control of the parameters affecting the crystal growth process. In particular, the aim is to induce the nucleation at supersaturated conditions close to the solubility boundary between labile and metastable regions, by modulation of specific physical parameters. The detailed knowledge of the phase diagram is at the basis of the devices we have developed especially with the focus on Neutron Macromolecular Crystallography. The 1st generation instrument combines the use of temperature control and seeding and allows for grow of large crystals in crystallization batch. A crystallization batch in the metastable zone is seeded with small protein crystals. The seeds are maintained inside this region of the phase diagram for as long as possible by doing a temperature step each time the crystal solution equilibrium is achieved. The temperature steps are repeated until crystals of suitable size for diffraction measurement are obtained. The 2nd generation instrument adds new functionality to the first instrument thanks to a fluidic cell enabling to perform a temperature controlled dialysis crystallization experiment. The new crystal growth apparatus combines accurate temperature control with control of the chemical composition of the crystallization solution and therefore it allows very sophisticated experiments to be performed. Systematic phase diagrams in multi-dimensional space can be investigated using far less protein material than previously. We have demonstrated that it can be beneficial to provide sufficient scattering volumes for neutron studies that require large-volume well-ordered single crystals. Based on this macro-scale instrument we have also conceived a miniaturizing apparatus that allows precise control of the experiment parameters using microfluidics. The functional microfluidic chips integrating microdialysis with the volume less than 1 µL have been already successfully tested with model proteins. The microchips have multiple designs in order to achieve single or multiple crystallization experiments at the same time. They are transparent to X-ray radiation and allow performing in situ X-ray crystallography experiments at room temperature. The automated microfluidic pipeline we are setting up is expected to be useful in monitoring and controlling the crystallization processes of challenging biological macromolecules, such as membrane proteins. Preliminary experiments also show potential benefit for synchrotron serial crystallography that require uniformly-sized populations of microcrystals (10-20 µm), optimal for time-resolved serial crystallographic experiments.

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Keywords: neutron macromolecular crystallography, control of crystal size, temperature-controlled (micro)dialysis crystallization

MS41 Training computational method developers

Chairs: Dr. Marijana Dakovic, Dr. Martin Lutz

MS41-01

Developing new crystallographic software: how and what to do?

Juan Rodriguez-Carvajal¹

1. Diffraction Group, Institut Laue-Langevin, Grenoble, France

email: jrc@ill.eu

Crystallographic software is nowadays distributed and used worldwide. The incursion of commercial programs in the arena of crystallographic computing has had as a consequence that the number of crystallographers able to contribute to the development of new tools and algorithms for handling new problems seems to be diminishing. There are still many specialized areas, where crystallographic software development is still worthwhile, in which commercial companies are not too much interested due to the lack of a profitable market. New developers should be attracted to the field of open crystallographic computing and they should be aware of open-source existing crystallographic libraries in order to not reinvent the wheel. The availability of new high level languages, like Python, has facilitated a lot the possibility of making graphic user interfaces (GUI) and write quite compact useful programs. We do not have to forget that, if we want to enter into de core of the crystallographic and mathematical algorithms as well as the development of relatively large projects, the use of statically highly-typed compiled languages (like Fortran 95/2003/2008 or C/C++) is much more efficient in the long term [1]. After presenting existing open libraries, my views on scientific software development and how to proceed in crystallographic computing, in this communication I will review, as a detailed example, the current status of the library CrysFML [2] which is the base for many crystallographic programs of the FullProf Suite [3]. CrysFML is a library written in Fortran 95 containing modules with plenty of procedures for elaborating crystallographic programs. A series of high level procedures are available so that the programming of relatively complex problems can be done easily. Some examples will be described. The library is open source (LGPL licence) and it is at the web-site: https://forge.epn-campus.eu/projects/crysfml/repository. As projected plans for future improvements we intend to develop a wrapper of the library to make the high level procedures available to the C-language (and hence to Python). A future version, in Fortran 2008/2018, fully exploiting the object oriented paradigm is currently being developed.

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Keywords: scientific software, crystallographic computing, Fortran/C/C++ languages

Experiences developing and publishing a medium-sized software project: CrystFEL

Thomas White

1. Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany

email: taw@physics.org

CrystFEL [1,2] is a free and open-source suite of programs for processing data from "serial crystallography" experiments, starting from detector frames and ending with merged intensities ready to be imported into other packages such as CCP4 and PHENIX. As of June 2018, it has been in development for 81/2 years and publicly available for just over 6 years. About 100 journal articles involved its use and 25 people from 8 different institutions have contributed code, with many more people contributing useful ideas and feedback.

This talk will describe our experiences developing CrystFEL and making it available to crystallographers around the world. How can the complexities of scientific data processing and high-performance computing environments be managed for the best overall results? What is the best way to get new users started, or to make changes to the software without tripping up the more experienced? And how can we encourage users who have programming skills to become contributors?

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Keywords: serial crystallography, CrystFEL, XFEL

MS41-O3

Using Mathematica® as a platform for crystallographic computing

Stian Ramsnes1, Helge Bøvik Larsen1, Gunnar Thorkildsen1

1. Department of Mathematics and Physics, University of Stavanger, Stavanger, Norway

email: stian.p.ramsnes@uis.no

A comprehensive Mathematica® [1] package for crystallographic computations has been developed.

Complete representations of space groups (point groups) and cell transformations based on International Tables for Crystallography, volume A [2] together with scattering factors from International Tables for Crystallography, volume C [2] and cross sections from xraylib [3] are built into the package.

Featured functionalities include calculation of structure factors, linear absorption coefficients and various crystallographic transformations.

The crystal data used by the package is normally generated from external *.cif files.

The package comes with a dynamic documentation seamlessly integrated with the Mathematica system, including code, examples and options.

From the onset, minimal Mathematica experience is needed to make use of the package.

It may be a helpful supplement in research and teaching where crystallography and X-ray diffraction is essential.

Although Mathematica is a proprietary software, all the code of the package is open source.

It may easily be extended to cover user-specific applications

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It may easily be extended to cover user-specific applications.

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Keywords: Mathematica, crystallography, computation

MS41-O4

Using DIALS with DUI

Luis Fuentes-Montero1, Gwyndaf Evans1

1. Diamond Light Source Ltd, Oxfordshire, United Kingdom

email: luis.fuentes-montero@diamond.ac.uk

The DIALS User Interface (DUI) is a graphical user interface that is designed to make data processing with DI-ALS[1] more user-friendly and efficient. A key feature is a full history tree that keeps track of all steps of processing. Every position in the tree represents the execution of a DIALS command line with full record of the user-supplied parameters, and the results, which can be inspected with several visualisation tools. At any step, the user can either fork, proceed to the next command or navigate to another step without loss of information. This ability to keep track of different branches of data processing gives the user freedom to explore different hypotheses, such as the space group of the crystal.

The output and visualization tools in DUI are conveniently arranged in tabs that update their content when the user navigates the tree, allowing rapid comparisons to aid decision-making. Each tab provides a different view on the state at that position of the tree, from detailed log file output of the DIALS program and graphical reports to an interactive image viewer and a 3D reciprocal lattice viewer.

The image viewer has been redesigned for DUI to provide responsiveness alongside various image overlays that give information about the spots and experimental models. The reciprocal lattice viewer complements this by providing a view of reflection positions in reciprocal space. Together these tools provide a powerful means for identifying problematic cases that may not be so readily apparent from the graphs and statistics in the report and log files.

DUI is intended to be intuitive and immediately useful across a wide range of user expertise. Beginners learning about the integration process with DIALS will benefit from the ease-of-use of the GUI and the visualisation tools. Experts retain full control of the underlying DIALS programs and can use the history tree to test different ideas quickly.

In this presentation these features of DUI will be demonstrated with a rotation dataset from a macromolecular crystal. DUI is distributed to users as part of CCP4 7.0[2].



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[2] M. D. Winn et al. Acta. Cryst. D67, 235-242 (2011) "Overview of the CCP4 suite and current developments" [doi:10.1107/ S0907444910045749]

Keywords: data integration,graphical user interface,data processing,software,DIALS,CCP4,

MS41-05

Crystallographic Computing Schools training future software developers

Harry Powell¹

1. Harry Powell Crystallographic, London, United Kingdom

email: hrp1000@virginmedia.com

At the IUCr General Assembly and Congress in Geneva in 2002, several people were appointed to the IUCr's Commission on Crystallographic Computing ("CompComm"); a major part of their remit was "to do something rather than nothing".

It was recognised by CompComm at the time that there was no formal provision to apply the science of Crystallography to new software, particularly in small molecule and powder methods; all freely available software was developed either in existing groups or by people working independently who began with knowledge of either crystallography or programming (but rarely both).

The major result from the work of CompComm's new blood in Geneva was the Siena Crystallographic Computing School which was held before IUCr XX in 2005. Developers of major crystallographic software packages across the science (powder, small molecule and macromolecular) gathered together to interact with and pass on their knowledge to the next generation [1]. Since then, with the exception of 2014, CompComm has run these events before every IUCr General Assembly and Congress; the next is planned to take place in the Czech Republic in 2020.

In 2013, SIG9 of the European Crystallographic Association (ECACOMSIG, the Special Interest Group in Crystallographic Computing) held a similar event before ECM28 in Warwick [2]; part of the rationale was to "fill in the two years when no IUCr CompComm event took place". This has now been repeated in every non-IUCr year since then, and the fourth took place in Mieres, south of Oviedo this week.

I will discuss how the Schools are organised, how we fund them and how we try to make sure that they are relevant to as many students as possible.

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[1] https://www.iucr.org/resources/commissions/crystallographiccomputing/schools/siena-2005-crystallographic-computing-school [2] http://sig9.ecanews.org/sig9_warwick.html

Keywords: training, workshops, software

MS42 New approaches to structure solution by crystallography and CryoEM: computational features and new algorithms

Chairs: Prof. Isabel Usón, Dr. Tom Burnley

MS42-O1

Solving X-ray crystal structures with cryo-EM reconstructions

Airlie McCoy1, Randy Read1, Robert Oeffner1, Andrea Thorn2

1. Department of Haematology, Cambridge Institute for Medical

Research, University of Cambridge, Cambridge, United Kingdom

2. Rudolf-Virchow-Zentrum, Würzburg, Germany

email: ajm201@cam.ac.uk

Electron density from electron microscopy reconstructions has been used for molecular replacement phasing of x-ray crystal structures since the pioneering work on icosohedral viruses [1]. Both negative stain and cryo-EM images have been used. The method is useful when the EM reconstructions are lower resolution that the X-ray data, so that phase extension is required after molecular replacement. The refined, higher resolution structure may then be docked back into the electron microscopy reconstruction, where it may form part of a larger macromolecular complex. The methods for using electron microscopy reconstructions for models for molecular replacement have much in common with the so-called cross-crystal averaging methods standard to X-ray crystallography. However, there are some issues particular to their use, chief amongst which is accommodating scale factor errors in the reconstruction. Marked differences in the low resolution Fourier terms, and the presence of high internal model symmetry can also present challenges for molecular replacement. Recent optimizations of the Phaser [2] algorithms to improve molecular replacement with electron microscopy reconstructions will be discussed.

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Keywords: molecular replacement, electron microscopy, crystallographic methods

MS42-O2

Cryo-EM and X-ray crystallography as complementary methods for structure determination

Holger Stark

1. Department of Structural Dynamics, Goettingen, Germany

email: hstark1@gwdg.de

Single particle cryo-EM has recently gained a lot of attention because numerous structures of large biological macromolecular complexes have been determined at high resolution. The number of map depositions in the EMDB database is constantly increasing and structures of complexes are being published that represented evasive targets for X-ray crystallography for a long time. It is therefore timely to ask what are the differences in maps obtained by cryo-EM and X-ray crystallography? Are the quality standards the same for both methods? What are the requirements on the sample for successful structure determination either by X-ray or cryo-EM? Which technique works best for a given complex and how does the information content differ? These questions will be addressed in the presentation based on our studies of large macromolecular complexes like the proteasome, ribosome and spliceosome.

Keywords: cryo-EM, macromolecular complexes

MS42-O3

Shift fields: A new approach to refinement using non-atomic parametrizations

Kevin Cowtan1, Jon Agirre2, Stephen Metcalfe2

1. Department of Chemistry, University of York, United Kingdom 2. University of York, York, United Kingdom

email: kevin.cowtan@york.ac.uk

Model refinement is a key step in crystallographic structure solution, allowing an atomic model to be optimised to best explain the crystallographic observations and reconstruct the missing phases. The scattering density is usually described in terms of atomic parameters, however in macromolecular crystallography the resolution of the data is often insufficient to determine the values of those parameters for individual atoms. Stereochemical and geometric restraints are used to provide additional information, but produce interrelationships between parameters which slow convergence.

These problems arise because atoms are small and their scattering density hard to see at low resolution. One solution with a historical precent in existing methods is to uncouple the model from the atoms by attaching the model parameters to regions of the electron density map rather than to atoms. These parameters can move the density or change the local temperature factor to better explain the structure factors. The parameters may be optimized at higher or lower resolutions by simply varying the volume of the region used to determine the parameter shifts, creating a smooth distortion of the model which partially mitigates the need for stereochemical restraints. The resulting method has a wide range of convergence and can be applied at low resolution, which also makes the calculation many times faster than comparable methods. Potential applications include massive screening of molecular replacement models, initial refinement of models with domain motions, and potentially the use of electron density from other sources such as cryo electron microscopy (cryoEM) as a refinement model.



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Keywords: refinement, molecular replacement, macromolecular crystallography

MS42-O4

Building atomic models into electronmicroscopy maps with ARP/wARP version 8.0

Grzegorz Chojnowski¹, Philipp Heuser¹, Joana Pereira¹, Victor Lamzin¹

1. EMBL Hamburg, Hamburg, Germany

email: gchojnowski@embl-hamburg.de

Recent developments in instrumentation and data processing techniques enabled determination of cryo-electron microscopy (cryo-EM) maps at resolutions previously attainable exclusively by macromolecular crystallography (MX). Indeed, the number of cryo-EM reconstructions at a resolution better than 4.0 Å deposited in Electron Microscopy Databank, which in principle allows for automated *de novo* model building, is growing fast.

The ARP/wARP software has, for over twenty years, provided continuously advancing tools for MX structure determination [1]. Here we present recent developments of ARP/ wARP that enable building atomic models of proteins and protein-nucleic acid complexes into cryo-EM maps at a resolution better than 4.0 Å. An automated input map pre-processing has been introduced to assure desired level of map sharpening. The main-chain tracing routines for proteins and nucleic acids have been advanced to yield more reliable models with improved local stereochemistry [2] and their applicability has been specifically extended to the cryo-EM maps. A new protein sequence-docking algorithm has been developed building up on the fragmentation tree concept [3] and on graph theory approaches. While having been specifically developed for cryo-EM, the new sequence docking also provides improved performance for low-resolution MX cases. Finally, the implementation of a new method for building poorly defined loops in cryo-EM maps has helped reduce the fragmentation of the built model.

Initial tests on deposited cryo-EM maps have been particularly encouraging, and the obtained results will be presented and discussed.

The module for the interpretation of EM maps has been made available with the most recent ARP/wARP 8.0 release and access to remote computation is provided with the redesigned web server at https://arpwarp.embl-hamburg.de

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Keywords: Model Building, Refinement, macromolecular crystallography, cryo-EM

MS42-O5

Reference-based restoration of local contrast for cryo-EM density interpretation

Arjen Jakobi1

 Department of Bionanoscience, Kavli Institute of Nanoscience, Delft University of Technology, Delft, Netherlands (Holland, Europe)

email: a.jakobi@tudelft.nl

Improvements in detector technology and image processing algorithms have rendered single-particle cryo-EM capable of routinely delivering structures of macromolecular assemblies at near-atomic resolution, permitting building and refining of atomic models. Yet, the interpretation of cryo-EM density maps with atomic models often remains challenging due to specific properties such as inherent contrast loss and spatial variation in map resolution. Variations in map resolution, if combined with global contrast restoration procedures, may result in density maps with locally inappropriate sharpening levels that are prone to hamper or even misguide misguide atomic model building. We have recently suggested a reference-based sharpening procedure to restore local structural features in cryo-EM density maps more faithfully [1]. We here present this procedure and explore the conditions for which local sharpening provides benefits over global contrast restoration procedures. Based on a systematic analysis of local vs. global sharpening procedures using publicly available datasets from the EMDB we identify boundary conditions for which local reference-based contrast restoration can be effective tool for map sharpening. We will illustrate pitfalls in atomic model building resulting from map sharpening artifacts and we outline practical issues affecting optimal sharpening results. The presented procedures should help overcome common difficulties in map interpretation using high-resolution cryo-EM density maps.

MS43 Topological analysis of structures: algorithms and software

Chairs: Prof. Patrick McArdle, Prof. Vladislav Blatov

MS43-01

Distinguishing metal-organic frameworks

Senja Barthel¹, Eugeny V. Alexandrov², Davide M. Proserpio³, Berend Smit¹

- 1. Laboratory of Molecular Simulation, EPFL Valais Wallis, Sion, Switzerland
- 2. Samara Center for Theoretical Material Science, Samara
- University and Samara State Technical University, Samara, Russia 3. Dipartimento di Chimica, Università degli Studi di Milano, Milano, Italy

email: senja.barthel@epfl.ch

We consider two metal-organic frameworks as identical if they share the same bond network respecting the atom types. An algorithm is presented that decides whether two metal-organic frameworks are the same. It is based on distinguishing structures by comparing a set of descriptors that is obtained from the bond network. We demonstrate our algorithm by analyzing the CoRe MOF database of DFT optimized structures with DDEC partial atomic charges using the program package ToposPro.

References:

doi: 10.1021/acs.cgd.7b01663

Keywords: metal-organic frameworks, topological analysis



[1] Jakobi et al, eLife 6: e27131 (2017)

Keywords: cryo-EM, map sharpening, model building

MS43-O2

Computational prediction of MOF structures from the entire periodic table: AuToGraFS + UFF4MOF

Matthew Addicoat1

1. School of Science and Technology, Nottingham, United Kingdom

email: matthew.addicoat@ntu.ac.uk

MOFs are inorganic–organic composite materials built by combining individually stable building blocks. Dozens of inorganic connectors may be linked via a nearly infinite variety of organic molecules in hundreds of topologies, resulting in a plethora of possible structures. The accurate and low-cost prediction of these structures is important for guiding synthetic efforts toward applications.

To meet this need of providing high quality structures of arbitrary frameworks, we developed AuToGraFS: the Automatic Topological Generator for Framework Structures [1]. AuToGraFS is open-source software, which employs a database of SBUs to create framework structure models using topologies sourced from the Reticular Chemistry Structure Resource (RCSR).

An integral part of AuToGraFS is a MOF-specific extension to Rappé's Universal Force Field, UFF4MOF [2]. The UFF-4MOF extension to UFF contains parameters for all transition metal environments found in the Computation-Ready Experimental (CoRE) Database and specific parameters for paddlewheels, Zn₄O and M₃O building blocks. Hydrogen-bonded frameworks are also possible [3]. With these two tools, we produce highly accurate structures with less than 2% error on cell parameters, even on cells as large as 20,000 atoms.



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Keywords: Metal-organic frameworks, Covalent organic frameworks, AuToGraFS

MS43-O3

Complex approach to analysis of crystal structures based on unified topological model

Eugeny Alexandrov¹, Andrey Golov¹, Alexander Shevchenko¹

1. SCTMS at Samara University and Samara State Technical University, Samara, Russia

email: aleksandrov_ev1@mail.ru

We present a unified topological model for analysis of connectivity in crystal structures. In this model, we represent crystal structure as a periodic simple graph (net), whose vertices and edges have particular weights. The resulting weighted net combines connectivity of chemical species with their descriptors. This approach provides heuristic analysis of crystal structures, modeling crystal growth and physical properties of substances (e.g. ionic conductivity), and finding structural relations at different levels of crystal organization.

The descriptors characterize the overall net (e.g. topological type), structural groups (e.g. coordination symbol), interatomic contacts (e.g. length), and voids (e.g. radii). We also propose two groups of new descriptors for interatomic contacts and voids. The former group includes bond pathways and parameters of electron density at the bond critical point: the electron density $\rho(r_{cp})$, $\Delta\rho(r_{cp})$, density of potential and kinetic energy. The latter group contains area and volume of van der Waals spheres of atoms and channel systems (ChS) periodicity of ChS, hkl of ChS, porosity, radius of included and free spheres.

The following new algorithms are developed to use the descriptors within the model:

 scanning of Voronoi net (a net of vertices and edges of Voronoi polyhedra) for analysis of the channels and cavities in a crystal structure;

2) approximation of the elementary void by Voronoi polyhedron whose faces are shifted to the van-der-Waals surface;

3) searching for the accessible channels system;

4) splitting the structure net to subgraphs (ligands, clusters, homoleptic groups) and their topological analysis.

All the algorithms are implemented in the ToposPro package (<u>http://topospro.com/</u>).

Using the algorithms two new topological databases were created to be used in the screening and design of MOF structures: the database of structural building units (more than 5000 entries) implemented in the TORIS client (http:// topospro.com/software/toris/) and the database of cavities and channels in more than 14000 MOFs.

New algorithms and descriptors were successfully used for assessment of mechanical stability and adsorption properties of some breathing and rigid MOFs, checking for isomorphism of 502 MOF structures from the CoRe MOF database [1], and searching for structural relations of 11 new coordination polymers [2,3]. We discuss the applicability of the topological model for the development of crystallographic knowledge databases.

The authors thank the Russian Science Foundation (Grant No. 16-13-10158), the Ministry of Education and Science of the Russian Federation (Grant No. 1.6101.2017/9.10), and the Russian Foundation for Basic Research (Grant No. 17-57-10001).

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Keywords: Weighted net, coordination polymers, knowledge database

MS43-O4

Assigning transition metal oxidation states to entries in the cambridge structural database

Matt Reeves1, Peter Wood2, Simon Parsons1

- 1. Department of Chemistry, The University of Edinburgh, Edinburgh, United Kingdom)
- The Cambridge Crystallographic Data Centre (CCDC), Cambridge, United Kingdom

email: m.g.reeves@outlook.com

In coordination chemistry the concept of formal oxidation states is essential to the understanding of metal centre geometries and in the interpretation of corresponding chemical and physical characteristics. The Cambridge Structural Database (CSD) currently contains over 400,000 transition metal-containing entries,1 however only about half contain a specified oxidation state. Surveying and editing the remaining entries is far too resource and time intensive to be carried out manually. A system in which entries missing this information can be quickly analysed and rectified is particularly desirable. Procedures have already been explored that could potentially semi-automate oxidation state validation by using the Bond Valence Sum (BVS) Method.2 This method proposes that the valence of an atom can be determined using only knowledge of its bond lengths, atomic neighbours, and some predetermined constants.3

Here we present the implementation of BVS to the CSD through CSD python API scripts, discussing the strengths and limitations of the method. Testing of the BVS method against entries containing named oxidation states has already proved applicable to over 80% of entries with a 94% success rate across over 40,000 structures. We also explore the use of complementary methods for improved assignment confidence and greater applicability, addressing potential issues with the BVS method. A process in which ligand fragment charges are automatically assigned from computational formation energy calculations is discussed, resulting in a combined methods assignment success for over 90% of transition metal environments.

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Keywords: CSD, Python



Automatic identification of solvatomorphic series in CSD by CrystalCMP

Jan Rohlicek1

 Department of structure analysis, Institute of Physics AS CR, Prague 8, Czech Republic

email: rohlicek@fzu.cz

In the recent past, several different methods have been published to determine similarities of crystal structures based on the atomic or even molecular positions. These methods can be divided into two basic groups - methods that use so called fingerprints of the crystal structure [1], [2] and methods that directly compare atomic positions [3], [4]. In the first case, an appropriate fingerprint that reflects arrangement of atoms, for example pair distribution function, has to selected. Subsequently, the similarity between two structures is determined by the comparison of their fingerprints. In the second case, it is necessary to find a transformation between the compared structures, then to overlap them and to compare the deviations of the atomic positions. Finding this transformation between two crystal structures is the most difficult task but the great advantage of these methods. The CrystalCMP's [5] method is based, similarly to the xPac [6] and COMPACK [7] methods, on the comparison of a representative molecular cluster where one type of molecule, usually the largest one, is included. During the comparison, the molecular clusters of the individual crystal structures are overlapped and the similarity is calculated as the sum of average deviation of the centers of the overlapping molecules with the average angle between them. Program uses either semi-automatic mode for the comparison, where user has to define a small fragment of the central molecule that will be used for finding the transformation between molecular clusters, or the automatic mode, where the program finds this fragment itself. When the small fragment of the central molecule is known, the comparison can be calculated. After the development of the automatic method, the program was used to compare molecular packing of identical molecules in the whole CSD. First of all, the python script using CSD Python API [8] was used for finding series of crystal structures containing identical molecule in the unit cell. After that, CrystalCMP automatically compared the molecular packing in every series.

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Keywords: similarity, crystal structure, molecular packing,

MS44 Operando and in-situ crystallographic studies using powder diffraction

Chairs: Prof. Simona Galli, Dr. Gavi Vaughan

MS44-01

Functional hybrid materials: Contribution of in situ powder X-ray diffraction

Nathalie Guillou¹

1. ILV - UMR CNRS 8180 - UVSQ - Université Paris-Saclay, Versailles, France

email: nathalie.guillou@uvsq.fr

Some functional hybrid materials can be obtained only as polycrystalline samples and in that case, powder diffraction is essential to characterize them. The aim of this talk is to show how in situ powder diffraction is significant for a better understanding of their structure-property relationships. In order to synthesize "tailor made" compounds, they are crucial in the understanding of Metal Organic Frameworks (MOFs) crystallisation processes.[1] In situ diffraction is also used to follow their "breathing" effect, or the adaptability of the pore opening to accommodate guest species with drastic changes in unit cell volume, without any loss of crystallinity or bond breaking. This second aspect will be illustrated by the uptake of CO2 in MIL-53(Fe).[2] The use of a gas cell which allows samples contained in glass capillaries to be dosed with gas up to 60 bars on the ID31 beamline (ESRF) allowed the precise localization of the guests. Finally, the last part of this talk will be dedicated to in situ ball milling diffraction experiments carried out recently on the ID15A beamline (ESRF) on Phase Change Coordination Polymers (PCCPs), which allow high quality data collection for both PDF and Rietveld analyses.[3]

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Keywords: hybrid materials, X-ray powder diffraction, phase transition

MS44-O2

New insight into nanoparticle nucleation mechanisms from X-ray total scattering

Kirsten Marie Jensen¹, Andy Sode Anker¹, Mikkel Juelsholt¹, Emil Skaaning Kjaer¹, Troels Lindahl Christiansen¹

1. Department of Chemistry, University of Copenhagen, Copenhagen, Denmark

email: kirsten@chem.ku.dk

Despite decades of research into nucleation processes, very little is known on how nanoparticle formation during solvothermal synthesis takes places on the atomic scale. We have developed methods which allows using in situ synchrotron X-ray Total Scattering and Pair Distribution Function analysis to follow nanoparticle nucleation and growth in situ.1-2 In contrast to conventional crystallographic studies, PDF analysis gives structural information from non-crystalline species, allowing obtaining structural information on the atomic scale, all the way from precursor to the final nanoclusters during synthesis. We have furthermore shown how PDF allows obtaining detailed information on nanocluster structures with no long-range order on nanoclusters fundamentally different from bulk materials.3 Here, we use in situ PDF to study the formation of metal oxides in solvothermal synthesis. Metal oxide nanoparticles are used in numerous applications in e.g. energy conversion and storage, and synthetic control over structure, particle size and morphology is required in order to tailormake materials for new applications. Solvothermal synthesis in organic solvents, i.e. amines or alcohols, are known to give high control over particle size. However, despite the very broad range of applications, the chemical processes involved in the formation of metal oxides are not well understood. Several nucleation mechanisms have been proposed. such as the existence of pre-nucleation clusters and oriented attachment, however none of the current models take the actual chemical processes into account. Using X-ray total scattering, we deduce the atomic structure of prenucleation clusters, present in the processes just before the crystalline nanoparticles have formed. We show that the solvent and synthesis conditions have large influence on the nucleation parthway and the structure of the nano-scale clusters in the synthetic pathway.

Keywords: In situ, nanoparticles, Total Scattering

MS44-O3

The use of Principal Component Analysis for fast and efficient kinetic analysis of combined in situ X-ray diffraction and spectroscopic data

Marco Milanesio¹, Rocco Caliandro², Luca Palin³, Eleonora Conterosito³

- 1. Dipartimento di Scienze e Innovazione Tecnologica, Alessandria, Italy
- 2. IC-CNR, Bari, Italy
- 3. Università del Piemonte Orientale, Alessandria, Italy

email: marco.milanesio@uniupo.it

Combining in situ X-ray powder diffraction (XRPD) and spectroscopic data opened new avenues in the studies of solid-state reactivity and kinetics. The obtained dataset is complex and large and efficient methods of analysis are not available. Recently Principal Component Analysis (PCA) resulted suitable for the fast kinetic analysis of in situ XRPD data [1-3]. Real and simulated in situ XRPD data were analysed to unravel the potentialities and limitation of the approach. In the simulations, the changing parameters (weight fractions, lattice parameters and crystallite sizes of reactant and products) were varied, at first separately and then together to understand the capability of PCA to untangle the kinetic information in cases of different complexity. Finally, experimental isothermal and non-isothermal real case data were analysed by PCA to explore real world applications. Then real experimental data on a complex case, the Maya Blue pigment formation are presented. It is generally accepted that MB can be obtained by thermal treatment of a mixture of naturally occurring minerals as inorganic framework (typically containing palygorskite), and an indigo dye source. To unravel the features of the MB formation process in situ XRD/PDF data were collected, on several framework-dye couples, while in situ FORS, TGA and dye leaching experiments were carried out on preheated palygorskite/ indigo mixtures. Statistical PCA-based methods were exploited to efficiently and jointly extract the chemical information from the more than 1500 experimental patterns. MB formation starts below 110°C (from PDF analyses), reaching maximum reaction speed at 150°C (shown by XRD/ TGA). Above 175°C, peculiar reactions occur with color changes, a stronger sequestration of indigo into the channels and changes in the affinity for water (proved by leaching and FORS experiments). The cooling to RT resulted important in defining the penetration and degree of sequestration of indigo into the palygorskite channels. The different colors, hues and stability in ancient and modern MB can be now explained by the thermal history of each sample. PCA performed rather well in non-isothermal in situ studies, and it can be used both for on-line data monitoring to check experiment data quality, and to efficiently unravel the reaction coordinate to successfully carry out kinetic analysis in in situ XRPD/PDF and spectroscopic data.

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Keywords: In situ X-ray Diffraction, Kinetic analysis, Principal Component Analysis

MS44-O4

Kinetics of gas sorption by porous frameworks probed by sub-second synchrotron powder X-ray diffraction

Iurii Dovgaliuk¹, Vadim Diadkin¹, Yaroslav Filinchuk², Dmitry Chernyshov¹

- 1. Swiss-Norwegian Beamlines at the European Synchrotron Radiation Facility, Grenoble, France
- 2. Université catholique de Louvain, Louvain-la-Neuve, Belgium

email: iurii.dovgaliuk@esrf.fr

Numerous porous frameworks have been intensively investigated as promising materials for gas storage and separation, sensing, catalysis, magnetism, luminescence, drug delivery and other applications.[1] To date, the dynamic behavior and involved mechanisms of flexible porous materials still mostly rationalized by the structural differences between the thermodynamically stable structures of the initial (empty) and final (filled) states or by following adsorption at equilibrium conditions.[2, 3] Very often fascinating phenomena upon gas adsorption can be either not well-understood (e.g. the switching of the gas selectivity),[4] or missed out without in situ temperature/pressure variable experiments (e.g. negative gas adsorption).[5] The time-resolved observation of structural evolution during guest uptake may shed light on actual mechanisms, kinetic and thermodynamic parameters of the sorption processes.

In this work, we present the result of a kinetic experiment, where the adsorption of noble gases by nanoporous γ -Mg(BH₄)₂ has been probed via sub-second powder diffraction of synchrotron radiation. The combined analysis of fluorescent background and structural information from sequential Rietveld analysis has uncovered 3 time-dependent processes related to gas uptake and provided a quantitative characterization in terms of rates, kinetic models and activation energies. Adsorption starts form the gas uptake by initial γ -Mg(BH₄)₂ host structure and then followed by a formation of secondary phase with higher kinetic barrier. The third process was observed at high temperatures and long exposure time and can be tentatively associated with radiation damage of the sample.

Our result shows the importance of diffraction methods for the characterization of thermodynamics and kinetics of gas adsorption by porous frameworks; the used approach can be further developed for more complicated *in situ* experimentation, where diffraction data would help to untangle different processes superimposed in macroscopic probes.

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Keywords: kinetics, gas sorption, powder X-ray diffraction

MS44-05

Combining experimental and computational techniques to understand phase transitions of nucleobase adenine

Dubravka Sisak Jung¹, I. Halasz², D. McDonagh³, G.M. Day³

- 1. DECTRIS, Switzerland
- 2. Division of Physical Chemistry, Ruđer Bošković Institute, Croatia
- 3. School of Chemistry, University of Southampton, United Kingdom

email: dubravka.sisak@dectris.com

Monitoring phase transitions in-situ becomes increasingly difficult if the transitions feature a series of similar structures, and if the occurring phases cannot be isolated from the mixture. In these cases, complete powder X-ray diffraction (PXRD) need to be collected in a minimal number of steps and exhibit statistics and resolution that allow for structure determination and refinement. While these problems are successfully addressed at synchrotron beamlines, laboratory diffractometers are rarely fit for the task. One of the challenging samples is adenine, a small and rigid molecule that exhibits two polymorphs: one monoclinic (I) [1] and the other orthorhombic (II) [2]. Both polymorphs feature a layered structure, what makes their PXRD patterns similar and difficult to resolve when in a mixture. Both phases are bench-stable at room temperature, with polymorph IIbeing metastable, while at temperatures above 280 °C phase (I) transforms into (II) [2].

In this work, adenine phase transition is monitored in-situ using a laboratory diffractometer in the Debye-Scherrer geometry, equipped with a Mo source, a specially developed oven and two simultaneously operating detectors. In this way, 74° in 20 of high-resolution data could be collected in only two shots. The resulting PXRD patterns revealed two additional adenine phases: III and X. The phase III was obtained pure at temperatures higher than 350 °C. It was characterized as a disordered layered structure using the DISCUS program. At about 200 °C, several low-intensity peaks indicated a new phase, (X). Although these peak positions could be indexed with a triclinic cell of a favorable volume, the data did not allow for cell validation or refinement. To complement the diffraction study, crystal structure prediction was carried out for adenine using guasi-random sampling in a large number of space groups. This has generated a set of structures energetically close to the two known polymorphs. A few of these computer-generated structures could correspond to the phase (X) observed in the PXRD patterns. Calculations are ongoing.

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Keywords: in situ, X-ray powder diffraction, structure prediction

GI-MS45 Women in crystallography

Chairs: Dr. Julia Contreras, Dr. Annalisa Guerri

GI-MS45-01

The role of the Athena Swann initiative in supported women researchers

Eleanor Dodson¹

1. Department of Chemistry, York, United Kingdom

email: eleanor.dodson@york.ac.uk

This is an initiative to highlight the (rising) number of women working in the high pressure research field. We come from all domains (geology, biology, physics, chemistry...). Indeed, we are not many, but we are many more than many people think. We are building up a public data base of women under high pressure group. We are several scientist women who work in the high pressure field. http://www.lct. jussieu.ft/pagesperso/contrera/index-hp.html

We have also created a FB and twitter accounts for everybody to be able to follow updates:

h t t p s : / / w w w . f a c e b o o k . c o m / W H P -1731930103697127/?code=95036

The aim of our group is to provide the community with facilities to count with gender equality at any of the high pressure events and lists. It has also helped organizers of events and committees to have a fair gender representation and provide a great example of women in science and references to many women graduate students and postdocs in the audience. We are trying to get as visible as possible not to be complainers and neither to build up a "women" club, our goal is to bring awareness and make us think twice in order to create a fair gender community.

Keywords: Work-life balance, institutional support

GI-MS45-O2

Gender, race and age diversity in crystallography: the impact of john desmond bernal & dorothy hodgkin on our science today

Tom Blundell¹

1. Biochemistry, Cambridge, United Kingdom

email: tlb20@cam.ac.uk

Crystallography owes much to JD Bernal who in the 1930s extended its impact to biology, cements and water - a diversity of interests - and attracted a multidisciplinary and diverse group of scientists to Cambridge - not only crystallographers Dorothy Hodgkin, Max Perutz and John Kendrew, all later Nobel laureates, but also others with an interest in materials such as cements and water structure and dynamics. This first impacted on me when as an undergraduate in Oxford University in 1963 I selected a project with Professor Tiny Powell FRS in the Department of Chemical Crystallography and discovered Dorothy Hodgkin FRS there as well. As a politically motivated undergraduate and Chair of the Joint Action Committee Against Racial Intolerance (JACARI) in Oxford University, I had read JD Bernal's Social Function of Science and even dipped into the books of Dorothy's husband, Thomas Hodgkin, on the politics of Africa. However, I was not familiar with Dorothy's work on penicillin and Vitamin B12, for which she was awarded the Nobel prize in 1964, just as I joined the group full time. Dorothy's group was the international, multidisciplinary and gender diverse "hub" of Chemical Crystallography and this had attracted me to do a PhD in the Department. However I first learnt some basic crystallography and computing before joining her international group in 1967 - with Guy and Eleanor Dodson, Margaret Adams already there on insulin and later Liang Dong-cai, M. Vijayan and Ted & Heather Baker joining. I moved eventually to be Bernal Professor & Head of Department of Crystallography in Birkbeck in 1976. This research centre was Bernal's creation that had attracted Aaron Klug (later Nobel Laureate) and Rosalind Franklin (DNA structure) to join in the 1950s. I inherited a gender, race and discipline diverse department with Christine Slingsby, working on the structure of crystallins of the eye lens, and Beatrice Gorinsky on transferrins, making it easy to recruit Janet Thornton (now Dame & FRS), Julia Goodfellow (now Dame and recently VC of University of Kent) and Bancinyane Lynn Sibanda from Zimbabwe in 1978. As they say, "the rest is history"!

Keywords: Gender, Race, Diversity

GI-MS45-O3

Women in science, the long road to gender parity

Jose Luis Jorda Moret1

 Instituto de Tecnología Química (Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas), Valencia, Spain

email: jjorda@itq.upv.es

Women have been involved in the different fields of Science since the beginning of History. In 2700 BC the Egyptian Merit-Ptah, the first female scientist named in History, was described as "chief physician". In Babylonian Mesopotania, around 1200 BC, Tapputi-Belatekallim is considered the first chemist. In ancient Greece medicine, mathematics or astronomy were open to women, and Egyptian female scientists, mainly in Alexandria, were involved in applied chemistry, as Mary the Jewess, considered the first alchemist.

The arrival of the European Middle Ages (476 BC), together with the death of the philosopher, astronomer and mathematician Hypatia of Alexandria in 415 AD, changed the scene, almost completely obliterating the presence of women in science and culture during the following centuries.

In the 11th century, most of the first universities only allowed the presence of men as teachers and students. The University of Bologna was a rare exception, allowing female students since its founding in 1088.

Some small changes appeared during the 17th century, when women began to collaborate in research in natural sciences (mainly astronomy and botany).

The 18th century marked the beginning of the return of women to science when Laura Bassi earned the first female professorship at a European university, and women were accepted in many Universities and Academies of Sciences throughout Europe.

In the 19th century the University of Zurich became a European reference on women's access to higher education, the first woman was officially accepted at a Spanish University (1872), women began to obtain Doctorate Degrees in Sciences (Medicine in 1849 and Chemistry in 1874) and the University of Oxford created its first no-segregated lectures (1879).

Finally, in 1903 and 1911 Marie Curie received her two Nobel Prizes in Physics and Chemistry, unequivocally confirming the ability of female researchers to compete with their male colleagues.

Regarding crystallography, Kathleen Lonsdale joined in 1924 the new research group created by William H. Bragg at the Royal Institution, and in 1964 Dorothy Crowfoot Hodgkin was awarded the Nobel Prize in Chemistry for her work in crystallography. Nowadays, data suggest that around one third of the people who work in crystallography in the world are women.

However, according UNESCO, although the ratio of male and female researchers is becoming closer, parity still depends to a large extent on several factors (scientific field, country, employment situation...). Therefore, it is necessary to continue working to finally reach real gender parity in science.

Keywords: Science, Women, Parity

GI-MS45-O4

Celebrating women in crystallography through the Cambridge Structural Database

Suzanna Ward1, Matthew Lightfoot1

1. The Cambridge Crystallographic Data Centre, Cambridge , United Kingdom

email: ward@ccdc.cam.ac.uk

Women have been involved in the different fields of Science since the beginning of History. In 2700 BC the Egyptian Merit-Ptah, the first female scientist named in History, was described as "chief physician". In Babylonian Mesopotamia, around 1200 BC, Tapputi-Belatekallim is considered the first chemist. In ancient Greece medicine, mathematics or astronomy were open to women, and Egyptian female scientists, mainly in Alexandria, were involved in applied chemistry, as Mary the Jewess, considered the first alchemist.

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Keywords: Women, Crystallography, Database

GI-MS45-O5

Breaking Bias

Claire Murray1

1. Diamond Light Source, Didcot, United Kingdom

email: claire.murray@diamond.ac.uk

From conference invitations [2] to research grant peer review [3], there are endemic systematic and structural barriers to women succeeding in science and in crystallography. Crucially there is a seemingly abstract barrier called bias which prejudices people for or against one person or group, especially in a way considered to be unfair. There has been extensive research demonstrating that women will disproportionately suffer from the effects of bias and can even bias against themselves. An example of this in the public domain is the under-representation of content on Wikipedia about women (both real and fictional), where only 17.57% of biography articles are about women.

This talk will directly address the issue of biases (unconscious and conscious) and provide tools and suggestions to help overcome these biases. Simple actions like reviewing biases in the selection of speakers or the use of biased language will all ensure that crystallography is an inclusive and welcome environment for all scientists.

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Keywords: Crystallography, Women

GI-MS46 Contributions to and of crystallography

Chairs: Prof. Carlo Mealli, Prof. Sine Larsen

GI-MS46-01

Crystallography and materials science – some personal historical notes

Gernot Kostorz1

1. Department of Physics, ETH, Zurich, Switzerland

email: kostorz@emeritus.ethz.ch

Materials science - even long before the term was adopted in the 1960s - has always relied on crystallographic methods. Since real materials are usually far from crystalline perfection, it has been of particular interest to analyze scattering features related to deviations from the average structure as indicated by the position of Bragg peaks. Apart from Bragg scattering from small crystalline objects and polycrystalline, often multiphase materials, diffuse scattering and small-angle scattering have helped materials scientists to elucidate and understand the properties of "real crystals". Since the 1950s, X-rays, neutrons, and electrons have seen a considerable historical development as probes in condensed matter research, including sources, beam conditioning, sample environment, detectors, data acquisition and evaluation, and modeling. Some of the apparently everlasting issues of interest to materials scientists, e.g., multiple phases, nano-size objects, internal strains, textures, phase transformations and precipitation, plastic deformation, defects and diffusion, will be briefly addressed in the light of "then" and "now".

Keywords: materials science, history

GI-MS46-O2

The Role of CCP4 in Macromolecular crystallography

Eleanor Dodson¹

1. Department of Chemistry, York, United Kingdom

email: eleanor.dodson@york.ac.uk

I will discuss the role of CCP4 (UK Collabortive Computing Project 4) in the rapid expansion of structural biology laboratories in Britain and Europe during the 1980s. CCP4 helped provide state of the art software free of charge to the academic community. Developers agreed to follow a common style of organisation, and to use common formats and libraries. In exchange the project organisers provided support with maintenance and distribution. CP4 also stimulated education in the new techniques by an annual meeting, and by organising workshops.

References:

[1] Winn M. D. et al. (2011). Acta. Cryst. D, 67, 235-242. doi: 10.1107/S0907444910045749

Keywords: Software development, international collaborations, education

GI-MS46-O3

Notes on the development of crystallography in Germany with special respect to the use of neutrons

Gernot Heger¹

1. Institut für Kristallographie, RWTH, Aachen, Germany

email: renateheger@gmx.net

The crystallography in Germany is based on two major roots: Out of the field of Mineralogy, research activities at German universities started already in the 18th century which lead i.e. 1877 to the foundation of the "Zeitschrift für Kristallographic und Mineralogie" by P. Groth. This journal played a major role for the publication of important crystallographic results from international authors and still exists since 2010 under the title "Zeitschrift für Kristallographic – Crystalline Materials". Out of the field of Physics came essential contributions to the development of X-ray crystallography by German scientists: From the discovery of X-rays by W. C. Röntgen (Noble Price in Physics 1901) and the discovery of the diffraction of X-rays by crystals by M. v. Laue (Noble Price in Physics 1914) to the dynamical theory of X-ray diffraction by P. P. Ewald (Hablitation 1917).

A milestone for the practice of crystal structure determination was the publication of the first series of International Tables with the title "Internationale Tabellen zur Bestimmung von Kristallstrukturen" which were edited 1935 by C. Hermann (former Assistant of P. P. Ewald) together with W. H. Bragg (Noble Price in Physics 1915) and M. v. Laue. The IUCr (founded 1948) started a second series of "International Tables for X-ray Crystallography" 1952 and a third enlarged series of "International Tables for Crystallography" from 1983 on. In the 1960th many new crystallographic chairs were created at German Universities and research groups were established in the fields of mineralogy, physics, chemistry, biology and materials science. Crystallographic scientists were always interested to improve their experimental methods and, hence, made considerable contributions to the development of large facilities for the research using synchrotron and neutron radiation. Large facilities in Germany and with German participation (access for international users):

- Synchrotron radiation with instruments for crystallographic research: PETRA III at DESY, Hamburg; BESSY II at HZB, Berlin; ESRF, Grenoble.
- Neutron radiation with instruments for crystallographic research: FRM II at the Research Neutron Source Heinz Maier-Leibnitz, Garching; BER II at HZB, Berlin; ILL, Grenoble.

At the RWTH Aachen University a laboratory of crystallography (Institut für Kristallographie) was established 1963 with the appointment of Prof. Theo Hahn. His enthusiasm for the symmetry concept of crystallography made him an ideal editor of the third series of the "International Tables for Crystallography" (Vol. A) – 1972-2009. Research topics of the Institut für Kristallographie:

- · Crystal structure analysis and crystal chemistry
- Crystal physics (structure properties relation) and crystal growth
- · Methodical development of neutron instrumentation.

Actually, the Institut für Kristallographie is operating two single crystal neutron diffractometers at the hot source of the FRM II:

- HEiDi, crystal structure analysis with short wave lengths
- POLI, investigation of complex magnetic structures using polarized neutrons.

In the last years, many crystallographic laboratories and chairs disappeared at German universities. As a result a reduction of the level of crystallographic knowledge and competence on the side of theory as well as on the application of methods is becoming clearly visible.

Keywords: Crystallography, Germany, Neutrons, History

GI-MS46-O4

Crystallography in Turkey

Engin Kendi¹

1. Hacettepe University, Ankara, Turkey

email: engin.kendi@gmail.com

The first research laboratory in Turkey was established in the 1950s by the Swedish physicist Prof. Dr. Harald PER-LITZ as 'X-ray Crystallography Laboratory at Ankara University. In the mid 1960's started the X-ray crystallography studies, which used photographic single crystal data collection techniques. In 1970 a new laboratory for structural research was established at Hacettepe University in Ankara. The purchase of a CAD-4 diffractometer in 1992 attracted young scientists to do graduate work in X-ray crystallography. In 1999 a rotating anode X-ray generator was put in operation in the same department. After the purchase of Rigaku XRPD, in 2009 SWAXS system was established and nanostructure studies using HECUS SWAXS system have began.

Hacettepe University Crystallography Laboratory has become the leading centre of X-ray crystallography in the country.

Today from east (Dicle University in Diyarbakır) to west (Dokuz Eylul University DEU in İzmir) of Turkey many universities were equipped to several X-ray systems. In these laboratories Computational chemistry, particularly topological analyses of electron density-QTAIM studies, molecular spectroscopy etc.; Data mining studies on Cambridge Structural Database (CSD); Protein Purification and Structural Characterization studies ; Energetic materials; Semicrystalline Hydrogells; Structure solution studies on powder crystals; production, research and development studies of the nanostructured materials which can show interesting biophysical, physicochemical and physical (magnetic, electric and mechanic) properties were performed.

After these developments, in February 2001 TCA (Turkish Crystallographic Association) was founded and in August 2001, The European Crystallographic Association welcomed the Turkish Crystallographic Association as a new member . After that TCA has been accepted 53rd member by the IUCr in 2014 Canada Meeting.

The 25th European Crystallographic Meeting was organized in İstanbul in 2009. 880 delegates and 70 exhibitors were attended to the Meeting.

In the frame of IYCr2014 International Crystallography Year Activities, The Open Labs. organized in collaboration with UNESCO and IUCr and TCA were held in DEU, İzmir (2014) and Bilkent U., Ankara (2015). TCA organized a Course on Powder Diffraction for MS and PhD students. The course was held at the Hacettepe University. Furthermore crystallographic activities for schoolchildren performed to celebrate IYCr2014; Crystallography Day Istanbul Turkey (23rd May 2014) and Istanbul Crystal Growth Competition (March 10-April 18).

Keywords: Crystallography, Turkey

GI-MS46-O5

Early contributions of crystallography to the atomic theory of matter

Giovanni Ferraris1

 Dipartimento di Scienze della Terra, Università di Torino, Italy, Turin, Italy

email: giovanni.ferraris@unito.it

Efforts to explain the morphology of the crystals and their anisotropic properties played a basic role in investigating the "inside" structure of the matter. In 1665 R. Hooke (1635-1703) was able to explain the external shape of some crystals by relating it to close packing of spheres; the discovery in 1669 of double refraction in calcite by R. Bartholin (1625-1698) brought C. Huygens (1629-1695) to propose, in 1690, a structural model of this mineral based on packing of ellipsoids.

One century later R.J. Haüy (1743-1822) opened the way to modern crystallography and theories on the atomic structure of matter proposing that the structure of crystals is based on periodic arrays of integrant molecules [1]. In early XIX century, F.S. Beudant (1787-1850) and W.H. Wollaston (1766-1828) observed co-crystallization of compounds with "similar" chemical formulae and E. Mitscherlich (1794-1863) introduced the term isomorphism to indicate the close similarity of the crystals formed by compounds that can co-crystallize [2].

The above mentioned theoretical models and experimental results, obtained in the field of crystallography, played a crucial role in solving a basic question debated for about one century and aiming to establish a distinction between the "particles" that nowadays are known as atoms and molecules. Comparing two isomorphous compounds that differ in composition only for the nature of one chemical element (e.g., an arsenate and its analogous phosphate), Mitscherlich successfully determined the atomic weight of elements, thus supporting a necessary distinction between atoms and molecules.

A. Avogadro (1786-1856) knew very well the results achieved by crystallography, as testified by his four-volume treatise of physics published in 1837-1841. In fact, he dedicated the first volume of this treatise to the science of crystals. In particular, he gave great emphasis to Haüy's work of which he published the figures that show how the morphology of the crystals can be explained on the basis of an internal periodic array of particles named integrant molecules, a wording adopted by Avogadro [3]. Nowhere, in his numerous scientific and private writings, Avogadro mentions that he was inspired by Haüy's work. However, it looks hard to exclude that the image of integrant molecules filling crystals contributed to the formulation of Avogadro's hypothesis that, under the same conditions, equal volumes of gases contain an equal number of particles.

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Keywords: Haüy's theory, Isomorphism, Integrant molecule

GI-MS47 How to... take your next steps in crystallography

Chairs: Dr. Andrew Maloney, Dr. Chiara Massera

GI-MS47-01

Evolution of materials science. The crystal structure now central to drug product development

Patricia Basford1

1. Pfizer, Sandwich, United Kingdom

email: pat.basford@pfizer.com

This presentation will share the experience of a founding member of the Materials Science group at Pfizer, Sandwich; with a focus on the changes that have occurred within the drug product development process over the last few decades.

The Materials Science group was established, at the Pfizer UK site in the early 1990's. From one perspective it could be said that the focus still remains the same; to deliver a stable, crystalline solid form, so providing acceptable attributes that enable delivery of a reliable drug product to the patient. However, significant changes have occurred, in those early days the crystal structure was not even considered, now it is at the core of the materials science discipline, central in fundamental to the application of computational tools.

Less routine examples of how the crystal structure was key in explaining solid form properties will be presented; highlighting how this directly influenced decisions and provided confidence in progression of candidates.

Keywords: solid form, drug product development, crystal structure

GI-MS47-O2

Patenting polymorphs at the European Patent Office – an insider's view

Ilaria Goss1

1. European Patent Office, Munich, Germany

email: ilariagoss@gmail.com

A number of patent applications and opposition cases in sector HBC (Healthcare, Biotechnology and Chemistry, especially in the technical area of Heterocycles) of the EPO relate to solid state forms of chemical compounds, in particular of active pharmaceutical ingredients. Chemical compounds can exist in a variety of solid forms including:

- · amorphous solids
- · polymorphs
- · solvates including hydrates
- · salts
- · co-crystals

Different solid forms of a compound display unique physicochemical properties which can influence the manufacturability, processing, handling and intended use. For active pharmaceutical ingredients, particularly important are the thermodynamic stability and the bioavailability for poorly water-soluble drugs. Other properties may also be important including chemical stability, filterability or hygroscopicity. In practice, solid state screening seeks to find a form with an optimal balance of desirable properties. Further interest in the subject stems from the fact that solid state form inventions create intellectual property opportunities for originator and generic companies alike.

The present presentation aims at offering some guidance for the way how the EPO is dealing with applications relating to solid state inventions.

It is particularly focused on polymorphs.

Keywords: EPO, patents, legal requirements

GI-MS47-O3

From chemistry to crystallography or the joy of being crystallographer

Santiago Garcia-Granda1

 Department of Physical and Analytical Chemistry, University of Oviedo-CINN, Asturias, 33006, Oviedo, Spain

email: sgg@uniovi.es

Coming back to the end of my studies of chemistry, in 1980 almost 40 years ago, the crystallographic panorama was really different from what we have now. Direct Methods were really showing its real power in solving organic crystal structures and the structure of biological macromolecules were the big challenge. Powder methods were oriented to phase analysis. The development and use of Databases were very limited.

In this environment a number of young students graduates in chemistry oriented his careers to crystallography, myself among them. In my particular case, I was quite autodidact, using computer cards in the scarce facilities in Spain, and making my first crystal structures with CRYSTAN [1]. Then in my postdoc, in Nijmegen 1985-1987 with Paul Beurskens, I really experienced the flavour of a crystallography laboratory while working in the development of DirDif[2]. Since I felt myself part of the crystallographic community, of the family of the International Union of Crystallography, actively participating in meetings, committees and assemblies.

The Rietveld method [3] was a real step on the study of materials and drugs. The new synchrotron, neutron and electron sources made possible to extend the limits further than imagination. The advances in computational methods allowed to investigate more complex systems in shorter time and let crystallographic computer programs be accessible to all crystallographers or users of crystallography.

Following the personal experience and the extraordinary expansion of crystallography in the last 40 years, I shall give an overview on the opportunities for young scientist interested in crystallography and crystallographic methods.

My involvement in the IUCr activities, including the regional associations and the extraordinary impact of the International Year of Crystallography with all the activities promoting Crystallography all around the world. The IYCr legacy fund and program hopefully will revitalize the crystallographic community of the XXI century. Doubtless, the new generations of crystallographers, men and women, will continue the job of the pioneers at the beginning of the twentieth century and the expansion and splendour of Crystallography along the century to formulate the new role of Crystallography in the twenty-one century and beyond.

Acknowledgments. This work was financially supported by Spanish MINECO (MAT2016-78155-C2-1-R).

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Keywords: Chemistry, Scientific Profile, Teaching-Research

GI-MS47-O4

What a difference a carrier choice makes?

Dubravka Sisak Jung1

1. DECTRIS, Switzerland

email: dubravka.sisak@dectris.com

Having this in mind that crystallography has long overcome its basic definition, it is perhaps easier to grasp that a background in crystallography offers many career choices, and that one choice does not necessarily exclude the other. In other words, background in crystallography provides you with a good set of initial parameter set (skills) that can allow a stable (career) refinement. Where exactly your career will converge depends on your refinement skills and the restraints that you (pre)define.

I have started my career with a diploma in chemistry/crystallography, and my main focus was structure determination from single crystal data. Fifteen years later I count three careers, none of them focused on the single crystal diffraction:

- research in a pharmaceutical company (crystallographer)
- · basic research in crystallography (PhD student)
- business development, marketing and consultancy in a high-tech company (application scientist)

This career path features periodic alternations between academia and industry, what allowed me to extend my initial set of skills to intellectual property, teaching, good laboratory practice, X-ray instrumentation, scientific communications, marketing, spectroscopy, turbine blades for aerospace industry, cultural heritage, world airports and much more.

I am also an academic guest at the University of Zurich. I keep the International Tables of Crystallography on the desk in my study. Calculations are ongoing.

GI-MS47-O5

Crystallographic software for the next generation

Richard Cooper¹

1. Chemical Crystallography Lab, Department of Chemistry, University of Oxford, Oxford, United Kingdom

email: richard.cooper@chem.ox.ac.uk

Where can crystallographic computing take you in your career and what can you do about it? I will reflect on some advances and side-steps taken through a career where crystallographic software has been the common feature.

In your early career you will be learning useful skills, staying at the forefront of the field and keeping your options open for your next move. Developing crystallographic software can give you transferable skills and an in-depth knowledge of the fundamentals of the subject. With these skills, many crystallographic software developers move between quite different scientific problems during their careers.

I had no experience of crystallography or software development when I started an undergraduate research project developing methods for visualising and interacting with crystallographic data. I will present some lessons learned along the way and how I might plan and do things differently with the benefit of hindsight.

Keywords: software, careers, crystallography

GI-MS48 Education in crystallography

Chairs: Prof. Mike Glazer, Dr. Aleksandar Visnjevac

GI-MS48-01

Ask not what crystallography can do for you - ask what you can do for crystallography

Chiara Massera¹, Marijana Đaković², Annalisa Guerri³, Catharine Esterhuysen⁴, Serena Chiara Tarantino⁵

- 1. University of Parma , Parma , Italy
- 2. University of Zagreb, Zagreb, Croatia
- 3. University of Florence, Florence, Italy
- 4. Stellenbosch University, Stellenbosch , South Africa
- 5. University of Pavia, Pavia, Italy

email: chiara.massera@unipr.it

Promoting and spreading crystallography at all levels of education: that is the aim of GIG3 – The General Interest Group on Education in Crystallography - launched at the ECM in Basel in September 2016. The main objectives of GIG3 are the creation of a network for the efficient coordination of common activities and of new projects, and ultimately increasing the awareness of the general public about the existence, utility and versatility of crystallography as a field of study and application.

In this session some of the past and ongoing activities of the Group will be outlined and, more importantly, ideas and suggestions will be discussed on how to transform the Group's tasks into concrete initiatives.

Keywords: teaching, promotion, dissemination

GI-MS48-O2

Diamond light source's biggest outreach project: 1000 samples, 100 schools, 1 great big experiment

Claire Murray¹, Julia Parker¹, Laura Holland², Project M Team¹, UK Students and Teachers³

- 1. Diamond Light Source, Didcot, United Kingdom
- 2. Rosalind Franklin Institute, Didcot, United Kingdom
- 3. Secondary Schools, Nationwide, United Kingdom

email: claire.murray@diamond.ac.uk

Project M [1] is a large outreach project conducted by Diamond Light Source, designed to engage secondary school students in a real science experiment, investigate calcium carbonate formation and exploit the high throughput capabilities available at synchrotron beamlines.

100 secondary schools across the UK made 1000 samples of calcium carbonate, using equipment and resources provided in a project pack. The samples produced were sent to Diamond in preparation for the diffraction patterns to be collected in a single 24 hour experiment, in April 2017 on beamline 111. The calcium carbonate samples were synthesised using selected additives, including amino acids, which affected the polymorphs of calcium carbonate that were formed (calcite/vaterite) and the lattice parameters of the mineral phases, which will be identified, by students, in the diffraction patterns.

Beamline II1 at Diamond Light Source is a high resolution powder diffraction beamline equipped with automated sample changing facilities and a fast diffraction detector [2]. The speed of data collection and sample changeover enable 1000 high quality diffraction datasets to be collected from powdered capillary samples in a 24 hour period.

Project M has successfully engaged more than 1000 students (age 12-18) from all across the UK (from the Shetland Isles to the south coast) that may otherwise be unaware of Diamond Light Source and the research being carried out there. This presentation will describe the aims of the project and present details of the implementation, results and feedback from the project.

References:

[1] http://www.diamond.ac.uk/ProjectM/

[2] Parker, J.E., et al. (2010) Journal Of Applied Crystallography 44 (1), 102-110

Keywords: Outreach, Synchrotron, Diffraction

GI-MS48-O3

The IUCr OUP Book Series; overview and update

John helliwell¹

1. School of Chemistry, University of Manchester, Manchester, United Kingdom

email: john.helliwell@manchester.ac.uk

This presentation will document the IUCr Books and will allow ECA participants to discuss with John Helliwell their ideas for future books and authors. Since its inception about 20 years ago more than 60 book titles have been published and around 58,000 copies sold. The books published within the book series are commissioned in two categories:

- · Monographs on Crystallography
- · Texts on Crystallography

A diverse, highly experienced, membership has recently been assembled and is as follows:

- J.R. Helliwell (Chair, UK)
- · G. Chapuis (Switzerland)
- · J. Gulbis (Australia)
- R Herbst-Irmer (Germany)
- H. Maynard-Casely (Australia)
- · P. Mueller (USA)
- M. Nespolo (France)
- N. Yagi (Japan)
- X. Zou (Sweden)
- K.A. Kantardjieff (USA; ex officio as Chair of Commission on Crystallographic Teaching)
- S. Adlung (ex officio representative of Oxford University Press)

The income derived to the IUCr from these works, as ever, helps support our community events and conferences, especially bursaries for young crystallographers. Please do join in. The process for publishing a book is as follows. The IUCr OUP Book Series Committee considers proposals for new publications and makes recommendations to the IUCr Executive Committee and to the Delegates of the Oxford University Press (the body responsible for approving all publications handled by the OUP). JRH as Chair welcomes proposals for new books to be included in this Series. The details of the procedure to submit a proposal are described here: http://www.iucr.org/iucr/governance/advisory-committees/book-series/proposals and basically involves providing: (a) a presentation of the motivation, aims, scope, level, and readership of the proposed volume; (b) a detailed Table of Contents (with subheadings); (c) a short CV of the authors; (d) a sample chapter or part of a chapter; (e) a list of related books and brief comments on how they differ from that proposed.

Keywords: Books, Education, Research monographs

GI-MS48-O4

FAST training programme at synchrotron facilities by IUPAP-IUCr LAAAMP project

Michele Zema1, Sekazi K. Mtingwa2, Sandro Scandolo3

- 1. International Union of Crystallography, Chester, United Kingdom
- TriSEED Consultants, LLC, Hillsborough, NC, United States of America
- 3. International Centre for Theoretical Physics, Trieste, Italy

email: mz@iucr.org

Synchrotron Light Sources are the most sophisticated example of an open and multidisciplinary research infrastructure. They have revolutionized research in many science and technology disciplines, leading to a proliferation of facilities worldwide. These, in turn, have facilitated the creation of international scientific communities, improving education and creating new job opportunities, successfully contributing to the socio-economic development of countries and regions. Because of their high costs and multidisciplinary use, synchrotron facilities provide strong opportunities for integration through networking and cost-sharing, and promote multi-disciplinary collaboration with the wider global community, while promoting science diplomacy and peace at large. Thus, light sources have become prime enablers of scientific and technological progress and innovation.

The website lightsources.org has links to some 47 Advanced Light Source (AdLS) facilities in 23 countries in various stages of operation, construction or planning, with some regions being poorly represented (e.g. Latin America and the Caribbean and SE Asia) or not represented at all (Africa). Discussions have started towards the establishment of facilities in those regions, while learning from the experiences of the Brazilian LNLS and SESAME.

Within this framework, the IUPAP and the IUCr have developed a programme named *LAAAMP* (*Lightsources for Africa, the Americas, Asia and Middle East Project*), funded by the 2016-2019 ICSU Grants Programme, to promote AdLS-related science in such regions, and focusing on training young researchers, reaching out to professionals, and engaging the public and governmental officials in discussions about the role that AdLSs could play to improve their countries' educational institutions, economies, social structures, health and world competitiveness.

One of the main tasks of *LAAAMP* is the training programme for FAculty-STudent (FAST) teams from targeted regions (namely, Africa, the Caribbean, Mexico, SE Asia or the Middle East) to spend two months at partner AdLSs. The participation of a professor accompanied by his/her PhD student in the training programme makes the experience more challenging and rewarding for the awardees, and, at the same time, proves very efficient in terms of continuation of the activities even after the mobility period. Awarded FAST teams are requested to provide a description of the research conducted, including any resultant publications, and an evaluation of the non-scientific aspects of the visit. The programme also includes the possibility for awarded FAST teams, who have been successful during their first visit, to apply for continuing grants.

Details on the *LAAAMP* FAST training programme are at https://laaamp.iucr.org/calls.

Keywords: researchers' mobility, training, synchrotron

GI-MS48-O5

Crystallographic education in Kazan

Olga Lodochnikova1

 Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS; A.M. Butlerov Institute of Chemistry, Kazan Federal University, Kazan, Russia

email: lod_olga@mail.ru

The study of the basic concepts of crystal chemistry is a part of the curriculum of Kazan Federal University. Students of this university are studying at Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, where unique crystallographic equipment is available: two single-crystal diffractometers and one powder diffractometer. Third-year students come with a guided tour. They watch how the selection of samples suitable for single-crystal X-ray diffraction is carried out, and how do experiments conducting. At the same time, students assigned to synthetic laboratories are encouraged to grow good single crystals of their samples and return with them on the 4th year of study for a full research at a practical lesson. As a rule, 2-3 people from the group bring their samples, which's amount is sufficient for both single-crystal and powdered X-ray diffraction. The best single crystal is selected, then the experiment is conduct and data is collect to determine the parameters of the crystalline cell within the APEX program. At this stage, students master the concept of crystal systems. Next, the main experiment is launched. During the data collecting, students are invited to use the CCDC to search for X-Ray data for structural analogues of their coursework objects. At the end of the experiment, the entire group of students participate in the process of solving and refining the structure by the programs integrated into the APEX package: SHELXS, SHELXD, SHELXT. At this stage, students become acquainted with the concepts of crystallographic symmetry elements and space groups. Further, after successful refinement and obtaining the final cif file, a group of students proceed to work on a powder diffractometer and examine the same sample. The obtained experimental diffractogram is compared with the one calculated from the results of single-crystal X-ray diffraction and a conclusion is made about the polymorphic homogeneity (or inhomogeneity) of the sample. For memory of the workshop, students carry out a cif-file obtained directly with their participation, which they can view using the popular Mercury program. Practical work in the X-ray laboratory is a favorite among students, rapid definition of the structure and spectacular visualization of the received data is a kind of fascinating "trick", which they remember for a long time.

This work was carried out with the support of the Russian Government Program of Competitive Growth of Kazan Federal University.

Keywords: crystal chemistry, education, workshop

31st European Crystallographic Meeting • Oviedo, Spain 22-27 August

MS01 - Micro & nano crystals in MX

Chairs: Dr. Helen Ginn, Dr. Thomas White

MS01-P01

Theory and methods in phasing of microcrystals of biological macromolecules

Michele Cianci¹, Max Nanao², Thomas R. Schneider³, Andrzej Olczak⁴

- Department of Agricultural, Food and Environmental Sciences, Università Politecnica delle Marche, Ancona, Italy
- 2. Structural Biology Group, European Synchrotron Radiation Facility, Grenoble, France
- Hamburg Unit c/o DESY, European Molecular Biology Laboratory (EMBL), Hamburg, Germany
- Institute of General and Ecological Chemistry, Lodz University of Technology, Łodz, Poland

email: m.cianci@univpm.it

During the last decade, crystallography of microcrystals has become the method of choice for a large number of projects in structural biology. Still today, attempts to collect data from microcrystals of $5-20 \ \mu m$ at their longest dimension, require a dedicated strategy and multi-crystal data collection. While most of the crystal structures can be solved by molecular replacement, in many cases still experimental phasing from microcrystals is needed.

De novo determination of macromolecular structures requires accurate measurement of structure factors and thereby estimation of the phases from the crystals of the given specimen. The anomalous signal from naturally occurring (S, P, Ca, etc) or incorporated (Se, Hg, etc) anomalous scatterers, can be harnessed with a Single-wavelength Anomalous Dispersion (SAD) experiment. Today, the properties of new synchrotron and XFEL sources, or new long-wavelength tunable beamlines for microcrystals [1,2], optimization of the X-ray scanning routines, data collection and processing flows [3], new algorithms for data merging [4], allow to collect, in just few hours, a full data set with anomalous signal by merging data from more than hundred micro crystals collected thus enabling X-ray diffraction data collection and phasing in microcrystallography (Fig. 1) [5]. Moreover, by conducting an extensive survey of 115 PDB sulphur SAD depositions and testing the statistical distribution that these represented, a useful predictor for aiding experimental success using sulphur SAD was developed [6]. So, we will present the current state-of-art of theory and methods in our hands for data collection and phasing in microcrystallography of biological macromolecules.

Keywords: microcrystals, phasing, long wavelength

MS01-P02

Retinal isomerization in bacteriorhodopsin captured by a femtosecond X-ray laser

Przemysław Nogły¹, Tobias Weinert², Daniel James², Sergio Carbajo³, Dmitry Ozerov⁴, Igor Schapiro⁵, Gebhard Schertler¹, Richard Neutze⁶, Jörg Standfuss¹

- 1. Department of Biology, ETH Zurich, Zurich, Switzerland
- 2. Division of Biology and Chemistry, Paul Scherrer Institute, Villigen, Switzerland
- Linac Coherent Light Source, Stanford Linear Accelerator Center National Accelerator Laboratory, Menlo Park, United States of America
- 4. Science IT, Paul Scherrer Institute, Villigen, Switzerland
- 5. Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel
- 6. Department of Chemistry and Molecular Biology, University of Gothenburg, Gothenburg, Sweden

email: przemyslaw.nogly@biol.ethz.ch

Ultrafast isomerization of retinal is the primary step in photoresponsive biological functions including vision in humans and ion-transport across bacterial membranes. We studied the sub-picosecond structural dynamics of retinal isomerization in the light-driven proton pump bacteriorhodopsin using an X-ray laser. A series of structural snapshots with near-atomic spatial and temporal resolution in the femtosecond regime show how the excited all-trans retinal samples conformational states within the protein binding pocket prior to passing through a twisted geometry and emerging in the 13-cis conformation. Our findings suggest ultrafast collective motions of aspartic acid residues and functional water molecules in the proximity of the retinal Schiff base as a key ingredient for this stereo-selective and effcient photochemical reaction.

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Keywords: time-resolved crystallography, X-ray free electron laser, ultra-fast dynamics

MS01-P03

Serial synchrotron crystallography at EMBL PETRA III beamline P14

Johanna Hakanpää¹, Gleb Bourenkov¹, Ivars Karpics¹, Guillaume Pompidor¹, Isabel Bento¹, Thomas Schneider¹

1. European Molecular Biology Laboratory, Hamburg, Germany

email: johanna@embl-hamburg.de

Serial synchrotron crystallography (SSX) combines X-ray images taken from randomly oriented crystals, passed through the beam using diverse delivery methods, into a single dataset. The method requires a high-brilliance synchrotron source with a beam size similar to the sample size, an appropriate sample delivery method, a detector with sufficient frame rate and a data processing pipeline. SSX can act as a pre-screening method for XFEL experiments or a standalone experiment when crystal growth to larger size cannot be achieved, e.g. in vivo grown crystals. Proof of principle experiments (1) have shown the feasibility of the method.

Our SSX setup at the EMBL beamline P14 (PETRA III, DESY Hamburg) utilizes the tools of conventional crystallography, minimizing setup time and sample consumption. In situ experiments can be done in CrystalDirectTM plates, also in meso. Cryo-samples are mounted in loops or harvested from plates with the CrystalDirectTM Harvester. Generally, the sample size is a few microns. Data collection runs as series of helical line scans, typically a dataset is collected in a few minutes, depending on the size of the region of interest. Progression of the data collection is monitored throughout the experiment as on-the-fly calculated heat map, displaying the diffraction scores as estimated by program DOZOR (2).

The acquired diffraction images are sorted and bunched into sub datasets according to the DOZOR score. The sub datasets are processed in parallel as small rotation datasets with XDS and scaled using XSCALE. We have demonstrated the feasibility of the pipeline using 5-micron lysozyme crystals as test objects. Using an Eiger4M detector, a data set of 65120 images was collected at P14 in 3 minutes as an in situ experiment in a CrystalDirectTM plate. About 2000 sub datasets, each containing 5-10 diffraction images, were integrated and scaled to yield complete data to 1.7 Å resolution. The structure could be solved by molecular replacement and electron density maps were of good quality.

We have established protocols for sample delivery, data collection and processing, making the pipeline feasible to use without previous experience in serial crystallography. Alternating between serial and conventional data collections is user controlled. Beamtime for experiments at P14 can be applied for through the EMBL user program at https://smis. embl-hamburg.de.

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Keywords: serial synchrotron crystallography

MS01-P04

Design of BLo6-XAIRA, the new microfocus beamline for MX at ALBA

Damià Garriga¹, Nahikari González¹, Jordi Marcos¹, Josep Campmany¹, Carles Colldelram¹, Josep Nicolás¹, Judith Juanhuix¹,

1. ALBA synchrotron, CELLS, Cerdanyola del Vallès, Spain

email: dgarriga@cells.es

ALBA is a third generation 3-GeV synchrotron radiation facility built near Barcelona servicing worldwide academic and industrial users since 2012. It currently hosts eight operating beamlines, including one dedicated to Macromolecular Crystallography (MX), BL13-XALOC. Current expansion plans of the facility include further 4 beamlines, one of them being a specific microfocus MX beamline, BL06-XAIRA, now in design stage.

The scientific case for XAIRA includes two aims: 1) to provide a full beam with a size of $3 \times 1 \ \mu\text{m2}$ FWHM (h×v) and a flux of >3×1012 ph/s (250 mA in storage ring) at 1 Å wavelength (12.4 keV); and 2) to reach a wide range of energies, 4-14 keV, to support MX experiments at long wavelengths exploiting the anomalous signal of the metals naturally occurring in proteins (native phasing), which is enhanced in the case of small crystals.

To match these requirements, the design of the beamline foresees a powerful photon source, a 2.3-m long in-vacuum undulator device, and the optics system prioritizes a high beam spatial stability. A channel-cut monochromator (CCM) will be installed, followed by a vertically focusing mirror long enough to accept the variations of the beam height introduced by the monochromator. This way, thanks to the large demagnification factor, the parasitic excursion of the beam at the sample position will be kept within only 60 µm for the whole energy range, which greatly simplifies the alignment of downstream elements. A high flux operation mode will also be possible, at the expense of energy resolution, by using a multilayer monochromator. To minimise the loss of flux at the low energy limit, the air path will be reduced between the sample and the detector by means of a He cone, and the whole beamline will only include two vacuum windows, upstream and downstream the sample.

The beam size will be adjustable to the users needs, producing larger sizes by defocusing the beam, or closing the horizontal secondary source slits to obtain a smaller spot size at sample, down to $1 \times 1 \mu m2$. A high precision air bearing goniometer with vertical rotation axis will provide a stable alignment of micron-sized samples to the small beam.

With a state-of-the-art pixel array detector and automated sample mounting and data analysis, XAIRA will allow rapid sample screening and data collection of crystals, and it will support a broad range of advanced diffraction experiments using micron-sized beam, from raster scanning to serial crystallography.

Keywords: microfocus beamline, XAIRA, ALBA

MS01-P05

First steps towards routine serial crystallography at the VMX-i beamline

Juan Sanchez-Weatherby¹, James Sandy², Agatha Butryn³, Pierre Aller³, Halina Mikolajek², Mita Charles⁴, Allen Orville³, Thomas Sorensen²⁰

- 1. VMXI Beamline, MX Group, Didcot, United Kingdom,
- 2. VMXi Beamline, MX Group, Diamond Light Source, Didcot, United Kingdom,
- XFEL Hub, MX Group, Diamond Light Source, Didcot, United Kingdom,
- 4. GDA Team, Diamond Light Source, Didcot, United Kingdom,

email: juan.sanchez-weatherby@diamond.ac.uk

MXi is the most recent addition to the portfolio of macromolecular crystallography beamlines at Diamond Light Source. VMXi was built in place of the previously existing tuneable I02 beamline and was built as an entirely remote, high throughput in-situ crystallography beamline. The beamline operates in a fully automated fashion and the users input data collection parameters and evaluate results via a remote web interface. The beamline is in the initial phases of user operation but its unique optical properties and very high flux make it particularly well suited for serial crystallography. During the past few months, several proof of principle experiments have been carried out at VMXi in collaboration with members of the XFEL hub. These experiments highlight the scientific opportunities that this beamline will offer and enable us to shape the best model for the VMXi user program that better suits the needs of the user community. The results from these experiments will also provide the test bed for improving the autoprocessing pipelines needed for the high volume of data produced by this beamline and XFEL beamlines around the world. We will present examples of the different sample delivery systems tested, how the resulting data are collected and processed, and discuss the options of how the beamline could be best used by the growing UK XFEL community.References:



Keywords: in-situ, serial crystallography, multilayer monochromator

MS02 - From data collection to structure finalization: getting the most from your crystal

Chairs: Dr. William Shepard, Dr. Katherine McAuley

MS02-P01

Identification of contaminants with SIMBAD: A Sequence-independent molecular replacement pipeline

Adam Simpkin¹, Felix Simkovic², Jens Thomas², Martin Savko³, Charles Ballard⁴, Marcin Wojdyr⁴, William Shepard³, Daniel Rigden², Ronan Keegan⁴

- 1. University of Liverpool, synchrotron SOLEIL, Paris, France
- 2. University of Liverpool, Liverpool, United Kingdom
- 3. Synchrotron SOLEIL, Paris, France
- 4. STFC, CCP4, Oxford, United Kingdom

email: hlasimpk@liv.ac.uk

In protein crystallisation it is not uncommon for contaminant proteins to crystallise instead of the protein of interest. Solving structures with molecular replacement in such cases can be difficult since the search models, assumed to be similar to the protein of interest, are not necessarily related to the proteins that have actually crystallised. SIMBAD is a pipeline to solve crystal structures without prior sequence information that can provide a route to identify the presence of a contaminant in a crystal and lead to structure solution. Early users of SIMBAD have unearthed several examples of unintentional crystallisation of previously known and unknown contaminant proteins. Other successful user cases have highlighted the problem of the mis-identification of crystals, where a mix-up has occurred (e.g. swapped crystallisation trays) and a dataset has been incorrectly assigned as being a different target structure. In all of these cases, mis-directed efforts in attempting to solve the structure of the target crystal could have been avoided through the use of SIMBAD at the point of data collection or through more rigorous annotation and experimental assessment of the crystal prior to data collection.

Keywords: SIMBAD, MR, contaminants

MS02-P02

3-D analysis of X-ray mesh scans and data collection strategies for macromolecular crystallography

Alexander Popov1, Igor Melnikov1, Gleb Bourenkov2

1. ESRF, Grenoble, France

2. EMBL, Hamburg Outstation, Hamburg, Germany

email: apopov@esrf.fr

Data collection procedures at a modern macromolecular crystallography beamlines rely heavily on automated preliminary experiments and data collection strategy software. The standard methods commonly implement a classical beam bathed single-crystal experiment [1, 2]. Further developments of these methods are aiming in automating the design of optimal data collection strategies for complex multi- crystal experiments, sub-crystal diffraction and multi-positional data collection. Three-dimensional information about positions, dimension and relative diffraction strengths of crystals mounted in the sample holder is obtained via several low-dose two-dimensional raster scans at various orientations of the sample holder. Automated preliminary analysis of diffraction images is carried out in real time by the program Dozor, which identifies the presence of a diffraction pattern from a macromolecular crystal, estimates the diffraction signal and produces the list of candidate diffraction spot positions.. Based on the Dozor output, the program MeshBest [3] automatically determines the areas which belong to individual crystals as well as the areas of crystal overlap. Latest version of MeshBest analyses multiple mesh scans simultaneously and provides 3D information on the dimensions, centroid positions and integral diffraction quality of each crystal resolved on the holder. The best achievable result of data collection for each individual crystal is estimated by the program BEST [2], which now uses empirical 3D model of crystal shape delivered by MeshBest. The strategy-optimization method has been extended to take into account the variations in irradiated crystal volume with a spindle rotation. BEST predicts the diffraction intensity at any moment of data collection as a sum of diffraction intensities of crystal voxels taking into account the profile of the incident X-ray beam and the dose absorbed by each voxel. We will present development and applications of the methods which demonstrate feasibility of auotomated approaches and indicate a possibility of significant improvement in data quality in particular for membrane protein crystals grown in mesophase.

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Keywords: BEST, MeshBest, Dozor

MS02-P03

VMXi – A new fully automated *in situ* and serial crystallography beamline at the Diamond Light Source

James Sandy¹, Halina Mikolajek¹, Juan Sanchez-Weatherby¹, Thomas Sorensen¹

1. Diamond Light Source Ltd., Chilton, Didcot, United Kingdom

email: james.sandy@diamond.ac.u

The Diamond Light Source has a cohort of seven beamlines dedicated towards macromolecular crystallography (MX). The VMXi beamline is one of the most recent additions to this group of successful MX beamlines at Diamond. VMXi is a dedicated microfocus, high-flux, high-throughput beamline. VMXi has been designed to be a fully automated *in-situ* and serial crystallography beamline which breaks away from the standard MX user experience. Samples are delivered to the beamline and are imaged using a Formulatrix Rock Imager system. These images are viewed via the SynchWeb application which is already widely used for displaying experimental results.

Users can look at individual drops and mark either a region or a point where they would like to carry out an experiment. By applying simple parameters, the user can assign any number of experiments to a plate. Once all experiments are registered, the plate joins a queue and makes its way on to the beamline via a series of plate-handling robots. Plate transfer times have been optimised to minimise local heating effects on the samples. An internal plate storage hotel means that x-ray time is most optimally used by minimising shutter closed time. Samples are aligned using an image matching algorithm between images from the Formulatrix Rock Imager and visible light images collected on the beamline. Experiments are carried out and the experimental results are displayed in SynchWeb. Users are informed once data have been collected by an automated email service. At no point do users interact directly with the beamline. The beamline operates autonomously using the parameters that the user has specified.

We describe here some experiments carried out on the VMXi beamline, and validate the beamline as a place to quickly collect highly useful screening and experimental data, without having any manual interaction with the sample.

Keywords: VMXi, in-situ, beamline

MS02-P04

Quantum refinement of X-ray and neutron protein crystal structures

Octav Caldararu¹, Lili Cao¹, Francesco Manzoni², Esko Oksanen³, Derek Logan², Ulf Ryde¹

- 1. Theoretical Chemistry, Lund University, Lund, Sweden
- 2. Department of Biochemistry and Structural Biology, Lund University, Lund, Sweden
- 3. Europen Spallation Source Consortium, Lund, Sweden

email: octav.caldararu@teokem.lu.se

Combining quantum mechanics and molecular mechanics (QM/MM) is one of the most important methods of studying the structure and function of proteins. This approach can also be applied in crystallographic refinement, as the geometry restraints used in refinement are in the form of an MM force-field. Thus, the MM potential for a small part of the molecule (for example, the active site of an enzyme) can be replaced by a QM potential, which can result in local improvement of protein crystal structures. We have developed such a method, *quantum refinement*, implemented in the ComQum-X program, which integrates a quantum chemical software with a crystallographic refinement software.

We present several recent applications of quantum refinement on both X-ray and neutron protein crystal structures. Firstly, we show how quantum refinement can help in determining the composition and geometry of the active site in metalloenzymes. For example, quantum refinement supports a model of particulate methane monooxygenase (pMMO) with only one copper atom in the active site instead of the two that the structure deposited in the PDB contains. (Cao et al., 2018) Secondly, we show a protonation study of the active site of nitrogenase. Quantum refinement predicts the correct protonation state of the homocitrate residue (Cao et al., 2017) and suggests that the FeMo-cluster is fully unprotonated in the resting-state crystal structure. Furthermore, we show some applications of the more recently developed ComQum-U (Manzoni et al., 2018), which combines quantum chemistry with joint X-ray and neutron refinement. This is especially useful in refining structures of enzymes that catalyze reactions that occur with proton transfer, in which case the neutron data may be unclear in the active site. To this end, we apply quantum refinement on the crystal structure of substrate-free lytic polysaccharide monooxygenase (LPMO) and on the crystal structure of triose phosphate isomerase (TIM) in complex with an inhibitor.

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(2018). J. Appl. Crystallogr. Submitted

Keywords: quantum mechanics, refinement

MS02-P05

Present status of SPring-8 macromolecular crystallography beamlines

Hideo Okumura¹, Kazuya Hasegawa¹, Seiki Baba¹, Nobuhiro Mizuno¹, Hironori Murakami¹, Takashi Kumasaka¹, Kunio Hirata², Go Ueno², Masaki Yamamoto²

- 1. Protein Crystal Analysis Division, Japan Synchrotron Radiation Research Institute (JASRI), Sayo, Hyogo, Japan
- 2. Advanced Photon Technology Division, Riken SPring-8 Center, Sayo, Hyogo, Japan

email: okumurah@spring8.or.jp

At SPring-8, JASRI and Riken are collaboratively developing five beamlines dedicated to macromolecular crystallography. Each beamline shares to serve broad requests from beamline users and liaises to develop new applications for enhancing each characteristic property.

Undulator beamlines, BL41XU [1] and BL32XU [2], focus on cutting edge analyses exploiting high flux microbeam produced by high-magnification focusing optics. In BL41XU, the two step focusing achieved beam size of 2 µm \times 2 µm - 35 µm (H) \times 50 µm (V). The wide range of beam size allows both micro-crystallography and high-resolution data collection that makes efficient use of crystal diffraction volume. In addition to high-resolution analysis, ultra-high resolution (~0.4 Å) data could be collected by using higher energy X-rays in energy range of 20 keV to 35 keV focused by using compound refractive lenses. Meanwhile, BL32XU can provide the fine beam with typical horizontal size of 1 µm. This micro-beam is very suited to data collection from small crystals, especially membrane protein crystals grown in LCP that are important targets on the beamline. For such micro-crystals, we developed an automated data collection system, ZOO. It is performed in advance of multi-crystal data collection for microcrystals; the crystal alignment tool, SHIKA, provides 2D spot population map of raster scan, and KUMA program is a tool suggesting data collection strategy with mitigating radiation damage.

On the other hand, the bending magnet beamlines BL26B1/ B2 and BL38B1 are focused for automation and routine data collection exploiting stable and easily tunable beam. The humidifiers have been installed for the HAG (Humid Air and Glue-coating) mounting method [3], which involves a combination of controlled humid air and water-soluble polymer glue for crystal coating. By this technique, most protein crystals can be kept at room temperature and are able to be cryo-cooled under optimized humidity. In Situ X-ray diffraction instruments using crystallization plate have also been developing. This system consists of plate goniometer, robot arm for plate mounting and plate hotel.

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Keywords: synchrotron x-ray crystallgoraphy, macromolecular crystallography

MS02-P06

ContaMiner and *ContaBase*: Automated identification of unwantedly crystallized protein contaminants

Stefan Arold¹, Arnaud Hungler¹, Afaque Momin¹, Kay Diederichs²

- Computational Bioscience Research Center (CBRC), King Abdullah University of Science and Technology, Thuwal, Saudi Arabia
- 2. Fachbereich Biologie, Universität Konstanz, Konstanz, Germany

email: stefan.arold@kaust.edu.sa

Solving the phase problem in protein X-ray crystallography relies heavily on the identity of the crystallized protein, especially when molecular replacement (MR) methods are used. Yet, it is not uncommon that a contaminant crystallizes instead of the protein of interest. Such contaminants may be proteins from the expression host organism, protein fusion tags or proteins added during the purification steps. Many contaminants co-purify easily, crystallize and give good diffraction data. Identification of contaminant crystals may take time, since the presence of the contaminant is unexpected, and its identity unknown. We have established a webserver (ContaMiner) and a contaminant database (ContaBase), both available at strube.cbrc.kaust.edu.sa/ contaminer/, to allow fast MR-based screening of crystallographic data against currently 76 known contaminants from more than seven different expression systems [1]. Here we present the latest developments of ContaMiner. Novel features include use of UglyMol [2] for an interactive online visualization of electron density maps of MR solutions, the possibility for screening of 'custom contaminants', and features for improved speed and performances. We are currently using ContaMiner to scan all PDB entries with suspiciously poor refinement statistics, and will present the results obtained.

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Keywords: contaminant, molecular replacement, web server

MS02-P07

Ensembling for molecular replacement: making the most of your distant homologues

Ronan Keegan¹, Daniel Rigden², Stuart McNicholas³, Eugene Krissinel¹, Jens Thomas², Adam Simpkin³, Felix Simkovic², Martyn Winn¹, Keith Wilson⁴

- 1. CCP4, STFC Rutherford Appleton Laboratory, Didcot, United Kingdom
- Institute of Integrative Biology, University of Liverpool, Liverpool, United Kingdom
- 3. Synchrotron Soleil, Paris, France
- 4. YSBL, University of York, York, United Kingdom

email: ronan.keegan@stfc.ac.uk

In the process of structure determination from a macromolecular crystallography diffraction experiment, the most successful approach to solving the well-documented phase problem has been and remains Molecular Replacement (MR). Typically, MR exploits the structural similarity between proteins that are evolutionarily related to derive the necessary phases from a known structure for an unknown target. The majority of proteins in the Protein Data Bank (PDB) have been phased in this way and, as this database expands, the chance of finding a suitable homologue for use in MR increases. Despite its success, the method requires a high degree of structural similarity between the homologue and the target in order for it to act as a suitable proxy for the target's phases. Given the availability of several structurally-similar homologues, an ensemble of such homologues can help to reduce this sensitivity. In addition, the structural alignment of these models to generate an ensemble can reveal common structural motifs or cores that are likely to be also present in the target. We present here two recent developments in the CCP4 suite designed to generate and exploit ensembles for use in MR. MrBUMP [1], an automated MR pipeline, can retrieve, align and truncate sets of known homologues to produce a set of ensembles. Alternatively, where there may be only one suitable homologue available, AMPLE [2], originally designed to exploit the use of ab initio generated search models in MR, can also now make use of the CONCOORD [3] application to produce a set of ensembles from a single known homologue. In addition, we present a related development in the molecular graphics application, CCP4mg. Through integration with the MrBUMP application, CCP4mg can assist in the generation of ensemble models by enabling the user to visually inspect and interactively edit the structural models.

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Keywords: Molecular Replacement, Structure Solution, Macromolecular Crystallography
MS02-P08

Vagabond: a new project for macromolecular model refinement

Helen Ginn¹

1. Diamond Light Source, Ltd, Didcot, United Kingdom

email: helen@strubi.ox.ac.uk

Model refinement for biomolecular crystallography, at present, relies on a model defined in atomic x, y, z parameters and associated B factors . Vagabond is a new refinement project which revisits the concept of refining in torsion space (1), defining the model in terms of bond lengths, angles and torsion angles. This significantly reduces the number of parameters required to describe most of the structure. However, it also incorporates a novel model for expressing flexibility in a chemically sensible manner, and is capable of describing weird and wonderful atomic distributions which are not accessible from isotropic or anisotropic B factor models. The combination of these features leads to a reduction in overfitting and increased clarity of maps



References:

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Keywords: macromolecular, model, refinement

MS02-P09

Neutron protein crystallography at the Heinz Meier-Leibnitz Zentrum (MLZ): New developments and recent application examples

Tobias Erich Schrader¹, Andreas Ostermann², Michael Monkenbusch³, Bernhard Laatsch⁴, Philipp Jüttner², Winfried Petry², Dieter Richter³

- 1. Forschungszentrum Jülich, Jülich Centre for Neutron Science (JCNS), Garching, Germany
- Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München, 85748 Garching, Germany
- Institute for Complex Systems ICS, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany, 52425 Jülich, Germany
- Forschungszentrum Jülich GmbH, Engineering and Technology (ZEA-1), 52425 Jülich, Germany

email: tschrader@gmx.de

With the advent of new instruments (e. g. Imagine at HFIR, MANDI at SNS and BIODIFF at FRMII) neutron protein crystallography has seen a resurrection from past pioneering work. New sample environment options at the instruments and a growing user community have greatly enhanced the outcome of the existing neutron diffractometers optimized for large unit cells. Measurements at 100 K in a nitrogen gas-stream (cryostream) are now routinely possible at most neutron diffractometers. Efforts to increase the flux at the sample position and to reduce the background at the detector make it possible to measure smaller and smaller protein crystals.

At the instrument BIODIFF latest developments allow to tilt the crystal to a kappa-geometry without the need to take it off from the goniometer head keeping it constantly at 100 K. The neutron single crystal diffractometer BIODIFF at the Heinz Maier-Leibnitz Zentrum (MLZ) is especially designed to collect data from crystals with large unit cells. The main field of application is the structural analysis of proteins, especially the determination of hydrogen atom positions. BIODIFF is a joint project of the Jülich Centre for Neutron Science (JCNS) and the FRM II. BIODIFF is designed as a monochromatic instrument with a narrow wavelength spread of less than 3 %. To cover a large solid angle the main detector of BIODIFF consists of a neutron imaging plate in a cylindrical geometry with online read-out capability. With a radius of 200 mm and a height of 450 mm it covers a solid angle of approximately 2π with a spatial resolution of up to 125 um. An optical CCD-camera pointing at the sample position is used to quickly align the sample with respect to the neutron beam. The main advantage of BIO-DIFF is the possibility to adapt the wavelength to the size of the unit cell of the sample crystal while operating with a clean monochromatic beam that keeps the background level low. To illustrate the power of neutron protein crystallography, some recent application examples will be shown.

Keywords: Neutron, Monochromatic, Diffractometer

MS02-P10

ISOLDE: Bringing macromolecular model building to life

Tristan Croll¹

1. Department of Haematology, Cambridge Institute for Medical Research, Cambridge, United Kingdom

email: tic20@cam.ac.uk

While model building in atomic-resolution maps is a straightforward and largely automated task these days, achieving high-quality results at resolutions below $\neg 3 Å$ is far more challenging. The scale of this challenge is reflected in the stereochemical quality of deposited models, with outlier rates often 1-2 orders of magnitude higher than expected. Beyond about 3.5Å, analysis of deposited models shows no correlation between stereochemical quality and Rfree.

Historically, tools for interactive model building have been severely limited by the modest computational power of the average workstation, and as such were limited to simple visualisation and (more importantly) relatively simple stereochemical restraints. In general, only direct bonded interactions (bond lengths, angles and torsions) were considered, relying heavily on the density map to provide the remain ing information necessary to precisely position individual atoms. Today, however, even a modestly-priced "gaming" laptop is capable of high-framerate 3D rendering of complex scenes, while the advent of massively-parallel GPU computing has dramatically increased the speed at which many computational tasks can be performed.

ISOLDE is a new interactive model-building environment designed to make maximum use of this explosion in computational resources to ease the task of low-medium resolution model building. Almost all manipulations of the model take place as interactive molecular dynamics simulations (composed of any arbitrary subset of the modelled atoms) which explicitly include all non-bonded van der Waals and electrostatic interactions, such that every movement of an atom automatically leads to accommodating movement of its surroundings. Simulations may be guided by direct tugging on atoms or by interactive addition/removal of position, distance and/or dihedral restraints (or their combinations as rotamer or secondary structure restraints). This approach ensures that the model is always settling towards low-energy conformations, effectively helping to "fit itself" as the user manipulates it.

A key design philosophy behind ISOLDE is to reduce the time involved in the adjust-validate-adjust cycle by providing, wherever possible, real-time structure validation as markup directly on the model. This is currently implemented for Ramachandran, rotamer and peptide omega validations: these are re-calculated with every coordinate change, with clearly-identifiable indicators appearing directly on or adjacent to problematic residues.

In this talk I will demonstrate the key features of ISOLDE and show some real-world examples of its use, and discuss some new features currently in planning.

References:

Croll, T. I. (2018). Acta Cryst. D74. In press

Keywords: model building, refinement, low resolution

MS02-P11

How can data collection affects the success of solving crystal structures using Singlewavelength Anomalous Dispersion?

Maria Jose Garcia Bonete1, Gergely Katona1

1. Dept. Chemistry and Molecular Biology, Gothenburg, Sweden

email: maria-jose.garcia.bonete@gu.se

Nowadays, different techniques exist to study macromolecular structures, however, X-ray crystallography still being one of the more powerful technique to obtain atomic structural information. Crystallography has two main limitations - obtain crystals and solve the phase problem. Even the data collection and analysis methods have highly improved in the last decades, the phase problem can be critical if there is not a model with high similarity for molecular replacement. SAD/MAD are the second approach after MR to succeed solving the phase problem. These techniques require a tunable X-ray beam and the presence of an atom in the crystal that absorb X-ray radiation and produce anomalous signal, such as Se, S, Zn⁺²... In this study, we analyze two different SAD data collection approaches to increase the success of direct methods for phase determination - continuous collection and inverse-beam geometry (where Friedel's pairs are collected close to each other avoiding radiation damage effect). This analysis has been done using crystals from the well study egg-hen lysozyme and the human protein survivin, which test the methods when the resolution and the diffraction are not optimal. In addition, a pairing reflections analysis using Bayesian inference has also been done. Our preliminary results show that inverse-beam geometry collection not only does not improve phasing but can also make it difficult to solve the structure when the collection is not optimal. Moreover, the use of bayesian inference for reflection pairing looks to improve the further data analysis.

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Keywords: SAD, phasing, data-collection

MS02-P12

New tools for serial crystallography: SPIND - sparse pattern auto-indexing and DatView - exploring and optimizing large multi-crystal datasets

Nadia Zatsepin¹, Chufeng Li¹, Natasha Stander², Xuanxuan Li³, Richard Kirian¹, Haiguang Liu⁴, Petra Fromme², John Spence¹

- 1. Department of Physics, Arizona State University, Tempe, United States of America
- School of Molecular Sciences and Biodesign Center for Applied Structural Discovery, Arizona State University, Tempe, United States of America
- Complex Systems Division, Beijing Computational Science Research Center and Department of Engineering Physics, Tsinghua University, Beijing, China
- Complex Systems Division, Beijing Computational Science Research Center, Beijing, China

email: nadia.zatsepin@asu.edu

We present two new tools for making efficient use of serial femtosecond crystallography (SFX) data. A large fraction of SFX patterns from microcrystals of large macromolecules contain fewer than 15 Bragg spots and are often discarded by existing autoindexing algorithms. SPIND is a reference-based algorithm for auto-indexing sparse, snapshot serial crystallography data with as few as 5 Bragg spots, using a known unit cell [1]. We demonstrate the suitability of SPIND for indexing sparse inorganic crystal data and for improving the quality of SFX data from two G protein-coupled receptors.

We have also developed DatView, a tool for exploring correlations in, and optimizing merged reflection lists from, large serial crystallography datasets. Stochastic fluctuations in microcrystals and X-ray free electron laser pulse parameters lead to orders of magnitude variability in measured intensities from equivalent reflections, which necessitated large SFX datasets for accurate merged structure factors. Numerous improvements in sample delivery, detectors and, critically, data analysis (including geometry optimization, orientation refinement, scaling and post-refinement), have significantly decreased the required number of indexed SFX patterns for structure determination. However, large SFX datasets (collected from thousands of microcrystals at room temperature) now allow users to not only select an optimum subset from potentially anisomorphous microcrystals for more accurate structure factors, but, importantly, it enables the quantification of microcrystal variability and sensitivity to experimental environment such as temperature and humidity, and offer insights into protein flexibility.

SPIND and DatView are written in Python and available via zatsepinlab.atlassian.net

References:

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Keywords: serial femtosecond crystallography, dataset optimization, clustering

MS02-P13

Collecting best data for meaningful structures

Andreas Förster¹, Claudio Klein², Clemens Schulze-Briese¹

1. DECTRIS Ltd., Switzerland

2. marXperts GmbH, Germany

email: andreas.foerster@dectris.com

Data collection is the last experimental step in a crystallographic project. All subsequent procedures (phasing, model building, model refinement) critically depend on the quality of the collected data. No amount of computational wizardry will turn poor data into a great model that can provide reliable biological insight.

With their intrinsic lack of noise, high dynamic range, small point spread and fast frame rates, modern Hybrid Photon Counting (HPC) detectors like PILATUS3 and EIGER enable the collection of data of exceptional quality. To fully exploit the power of these detectors, the user has to design her collection strategy based on the underlying technology.

In this presentation, we will explain why HPC data should always be collected with a small crystal oscillation increment per image (relative to the crystal mosaicity). This strategy is known as fine phi-slicing. We will also explain why HPC technology favors high multiplicity experiments. Native SAD structures determined at room temperature and from a crystal in space group P1 will illustrate the power of these two approaches.

Small oscillation increments minimize the background measured with each reflection, thus increasing signal to noise. High multiplicity decreases the systematic errors of the experiment and brings integrated intensities closer to the real value. Both strategies have long been known in theory to lead to the most accurate data possible. In practice, technological hurdles like detector readout noise and dark current and detector readout time have forced the user into compromises in the past, balancing what's best for the crystal with the constraints of the detector.

With HPC detectors, everyone can collect data optimally. This doesn't mean every experiment is a success. It still has be set up right. Keeping the points in this presentation in mind, trained crystallographers will not have to think twice to get the most from their crystals.

Keywords: Accurate data, Experimental strategy, Hybrid Photon Counting

MS03 - Combining methods in macromolecular structure determination, including special conditions MX

Chairs: Dr. Martin Walsh, Dr. Victor Lamzin

MS03-P01

BioSAXS at ESRF: The solution scattering Beamline BM29

Martha Brennich¹, Pernot Petra², Mark Tully²

1. EMBL Grenoble, Grenoble, France

2. ESRF, Grenoble, France

email: brennich@embl.fr

Small angle X-ray scattering (SAXS) is ideally suited to study the structure and structural changes of biological macromolecules in solution. The last decade has seen a surge of technological and conceptual development in small angle scattering that increased the importance of SAXS in the toolkit of structural biology. At the ESRF, the BioSAXS beamline BM29 is dedicated to solution scattering and optimized for routine measurements of biological macromolecules [1]. It aims at facilitating SAS for non-experts by providing easy and rapid access as well as reducing the effort to collect and assess data.

BM29 primarily offers two data collection modes: Bio-SAXS with a robotic liquid handling sample changer (SC) and BioSAXS with online size-exclusion chromatography (SEC). Both modes are highly automated and switching between modes is instantaneous. In both modes, primary data processing from azimuthal integration to determination of SAS invariants is completely automated and provides immediate feedback. The electronic logbook ISPyB collects all data and associates relevant meta-data. It assists the users in designing their experiments, in associating data with meta-data and in the primary assessment of data quality.

Here the experimental setups available on BM29 will be described together with the various examples of the Bio-SAXS data obtained. Recent examples of BM29 research, including the integration of microfluidics systems and online ion-exchange chromatography as well as the possibilities for new experiments in BioSAXS.

References:

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Keywords: SAXS, complementary techniques, instrumentation

MS03-P02

Flexible Fitting of Macromolecular Structures into Small-Angle Scattering (SAXS and SANS) Profiles

Sergei Grudinin¹, Alexandre Hoffmann¹, Anne Martel², Sylvain Prévost²

- 1. Univ. Grenoble Alpes, Inria, CNRS, Grenoble INP, LJK, Grenoble, France
- 2. Institut Laue-Langevin, Grenoble, France

email: sergei.grudinin@inria.fr

Large macromolecular machines, such as proteins and their complexes, are typically very flexible at physiological conditions, and this flexibility is important for their structure and function. Computationally, this flexibility can be approximated with just a few collective coordinates, which can be computed e.g. using the Normal Mode Analysis (NMA). NMA determines low-frequency motions at a very low computational cost and these are particularly interesting to the structural biology community because they are commonly assumed to give insight into protein function and dynamics.

We have recently introduced a new conceptually simple and computationally efficient method for *nonlinear* normal mode analysis called NOLB [1]. Overall, the NOLB method produces structures with a better local geometry compared to the standard techniques, especially at large deformation amplitudes, and it also predicts better structural transitions between conformational states of macromolecules. Finally, the NOLB method is scalable and robust, it typically runs at interactive time rates, and can be applied to very large molecular systems, such as ribosomes.

NMA can be combined with other computational techniques for various applications. I will specifically highlight our very recent flexible fitting methods for small-angle X-ray (SAXS) and neutron (SANS) profiles. This was made possible thanks to our SAXS and SANS packages called Pepsi-SAXS [2], and Pepsi-SANS [3], respectively. Pepsi-SAXS is a novel and very efficient method that computes SAXS profiles from atomistic models. It is based on the multipole expansion scheme and is significantly faster with the same level of precision compared to CRYSOL, FoXS and other methods. Similarly, Pepsi-SANS is our novel approach for computing SANS profiles. Recently, we designed a computational scheme that uses the NOLB nonlinear modes as a low-dimensional representation of the protein motion subspace and optimizes protein structures guided by the SAXS and SANS profiles. Overall, this scheme allows to significantly improve the goodness of fit to experimental profiles, has a very reasonable computational time, and produces plausible structural structural atomistic-level predictions.

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MS03-P03

Long-wavelength phasing at the P13 EMBL Macromolecular Crystallography beamline at Petra III

Guillaume Pompidor¹, Gleb Bourenkov¹, Isabel Bento¹, Johanna Hakanpää¹, Ivars Karpics¹, Thomas Schneider¹

1. European Molecular Biology Laboratory, Hamburg, Germany

email: pompidor@embl-hamburg.de

The P13 Macromolecular Crystallography beamline, operated by the EMBL at PETRA III, enables diffraction data collection over a wide energy range, from 4 keV to 17.5 keV (0.7 - 3.1 Å)[1]. In order to fully exploit the beamline capability at low energy (10^{12} ph.s⁻¹ at 5 keV), the PILATUS 6M-F detector, with a 450 mm Si sensor thickness and with a custom calibration at low energy, is mounted on a 2 q-angle stage to increase the maximum resolution achievable (2.4 Å at 4keV).

We will present and describe the typical experimental setup for long wavelength data collection. For low-energy experiments, typically below 5.5 keV, the air absorption can be drastically reduced by the use of a helium path. The gas is circulating inside the detector and in a homemade cone, which can be fixed on the detector upon user request. The beamline can be setup for low-energy data collection in about 10 minutes and remains fully compatible with the use of the sample changer, for high-throughput screening, and the mini-k of the MD2 diffractometer allowing the reorientation of the crystal for optimized anomalous data collection.

Several examples of structure determination using intrinsic anomalous scatterers, such as sulfur (SAD) or calcium (MAD at the Ca K-edge at 4.05 keV) will be presented. We will especially demonstrate the efficiency of the He-path in the improvement of diffraction data quality at low energy.

To extend the experimental opportunities, a small laboratory dedicated to the preparation of derivatives is available to users. With more than 150 compounds available, the heavy atom library contains many elements (Cd, Pd, U...) exhibiting strong anomalous signal at low energy, which are excellent candidates for SAD and MAD experiment at long wavelength.

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Keywords: Long-wavelength phasing

MS03-P04

Simultaneous XRD and XES at XFELs, elucidating electronic and geometric structures of metalloproteins

Roberto Alonso Mori1

1. SLAC National Accelerator Laboratory, Menlo Park, United States of America

email: robertoa@slac.stanford.edu

One of the fields where the advantages of X-ray free electron lasers (XFELs) have proven to be very fruitful is in the study of metalloproteins(1). These proteins, where metal centers efficiently catalyze chemical processes under ambient conditions, are ubiquitous in nature. X-Ray diffraction (XRD) has become a standard technique in synchrotron radiation (SR) sources worldwide to elucidate the geometric structure of crystallized proteins, and X-ray spectroscopic techniques to provide information about the electronic structure of the active site. Despite the enormous progress of the field achieved from SR-based measurements, these studies suffer from some experimental constraints, the main being the radiation-induced damage of the sample by the X-rays, which makes it difficult to collect the signal from the intact sample for radiation-sensitive systems.

At XFELs, each fs X-ray pulse is short enough to probe the sample and yield a detectable signal outrunning the SR-type radiation damage (in the ps) scale. The consequence is the possibility to measure sensitive systems under ambient, and therefore, functional conditions. The short X-ray pulses also allow the study of these processes in real time by following the catalytic reactions and the associated electronic and geometric changes step by step with fs time resolution. In this presentation I will describe the methods developed in the past few years at XFELs to study metalloproteins and discuss some examples and applications. In particular I will emphasize how X-ray emission spectroscopy can be used as an in situ method for monitoring the integrity of metal catalytic centers during simultaneous XRD data collection(2).

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Keywords: XES, Spectroscopy, XFEL

MS03-P05

Effect of pressure on the crystal structure and adsorption of β-lactoglobulin

Katarzyna Kurpiewska¹, Artur Biela², Joanna I. Loch¹, Sylwia Świątek³, Barbara Jachimska³, Krzysztof Lewiński¹

- 1. Jagiellonian University, Department of Crystal Chemistry and Crystal Physics, Faculty of Chemistry, Kraków, Poland
- Jagiellonian University, Bionanoscience and Biochemistry Laboratory, Małopolska Centre of Biotechnology, Kraków, Poland
- Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Kraków, Poland

email: kurpiews@chemia.uj.edu.pl

 β -Lactoglobulin (LGB) is of a huge importance to the food industry mostly because it is a principal whey protein [1]. Since pressurization is gaining a particular interest as an alternative procedure for milk products processing the pressure effects on this small protein has been extensively studied by the food community [2]. Wide range of methods was used to characterize biochemical properties of β -lactoglobulin after or during pressurization [3].

Presented studies concern the analysis of the β -lactoglobulin conformation observed in the crystal state determined at pressure 430 MPa. Structural changes in high pressure LGB structure revealed by X-ray diffraction were correlated with the physicochemical properties of pressure-treated β -lactoglobulin examined by dynamic light scattering, electrophoretic mobility and quartz crystal microbalance with dissipation monitoring measurements.

Examination of pressure effects on the conformation of LGB has shown that it is possible to observe starting stages of dimer dissociation under pressure of 430 MPa in the crystal state. Additionally, a number of local and global changes within a protein molecule has been identified as a result of pressure perturbation. Comparison of ambient and high pressure β -lactoglobulin zeta potential values and effectiveness of their adsorption onto gold surface allowed to propose and justify different scenarios of LGB adsorption (Fig 1.). Our results imply that modification of milk proteins for desirable functional properties requires careful selection of pressure-treatment conditions.

Acknowledgements: The research was carried out with the equipment purchased thanks to the financial support of the European Regional Development Fund in the framework of the POIG Program (contract no. POIG.02.01.00-12-023/08) and grant NCN OPUS 2012/07/B/ST5/00767



Fig.1 Model of a different pathway constant in U28 advergence on the gold nulfand for station protect and for protect presentant of to 200 MPs (after decompression).

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Keywords: high pressure protein crystallography, adsorption, β-lactoglobulin

MS03-P06

Unreduced enzyme intermediate structure caught by X-ray Free Electron Laser

Peter Moody¹, Hanna Kwon¹, Emma Raven¹, Takehiko Tosha², Hiroshi Sugimoto², Keitaro Yamashita³

- 1. Leicester Institute for Structural & Chemical Biology, University of Leicester, Leicester, United Kingdom
- 2. Riken SPring-8 Center, Japan
- 3. University of Tokyo, Japan

email: peter.moody@le.ac.uk

The heme peroxidases have high valent ferryl (Fe(IV)) intermediates, these intermediates can be spectroscopically monitored, formed and cryo-trapped in the crystal, and thus the structures determined. However, X-rays are strongly reducing and therefore standard X-ray crystallographic data collection methods are likely to perturb the chemical nature of these intermediates. We are particularly interested in the "Compound II" intermediate, and determining if its identity is Fe(IV)=O or Fe(IV)-OH. These should be distinguishable from the Fe-O distance, but direct or indirect photo reduction into the ferric state would make these measurements invalid. By using fs flashes of X-rays from the free electron laser SACLA at Spring-8 to record diffraction data before photoreduction can take place, we have been able to determine the structure of the unreduced Compound II intermediate of Ascorbate Peroxidase at 1.5Å. The data collection methodology will be presented. The preliminary refinement results will be discussed in the context of our results from neutron crystallography and previous multiple crystal approaches.

MS04 - Biophysical characterization and crystallization

Chairs: Dr. Andrzej M. Brzozowski, Dr. Pavlina Rezacova

MS04-P01

Magnetic crystallization proof-of-concept: Lysozyme and trypsin case study

Raquel dos Santos¹, Iana Lychko¹, Maria João Romão¹, A. Cecília A. Roque¹, Ana Luísa Carvalho¹

 Ucibio, Requimte, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal

email: rar.santos@campus.fct.unl.pt

Iron oxide magnetic particles (MPs) affinity fishing is a proven method for target protein separation from crude extract [1]. Given the virtual infinite surface modifications that can be made on magnetic particles surface, we investigated the MPs influence in protein crystal growth as nucleation points. Functionalized and non-functionalized MPs were used as additives in lysozyme and trypsin crystallization in the presence and absence of an external magnetic field. A rational design for MPs functionalization was achieved, having MPs functionalized with chitin for lysozyme crystallization, and MP functionalized with casein for trypsin. The physico-chemical properties of the MPs were studied by Fourier transform infrared spectroscopy, dynamic light scattering, zeta potential and transmission electron microscopy. The assay was developed to overcome some crystallization drawbacks as crystal growth kinetics, yield and morphology. Improvement of some of these factors were observed, notably in the presence of functionalized MP. The presence of functionalized MP led to a faster crystal growth kinetics, still improving crystal yield and morphology without hampering crystal diffraction. The new magnetic crystallization method enables the possibility to overcome some protein crystallization difficulties, but also, due to the MP functionalization system, has the potential to be integrated in protein purification methods involving crystallization/precipitation steps. For this purpose, a high throughput screen in the presence of MP functionalized with an affinity ligand towards antibodies was designed showing protein crystal growth in different crystallization conditions.

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Keywords: Magnetic particles, Novel crystallization method, protein crystallization

MS04-P02

Synthesis and Characterization of Cross-Linked Lysozyme Crystals filled with Single-Walled Carbon Nanotubes Bionanomaterials

Guillermo Escolano^{1,2}, Rafael Contreras-Montoya¹, Juan J. Díaz-Mochón³, Luis Álvarez de Cienfuegos¹, José A. Gavira⁴

- Departamento de Química Orgánica, Facultad de Ciencias (UGR), Granada, Spain
- 2. Laboratorio de estudios cristalográficos, Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), Granada, Spain
- Departamento de Química Farmacéutica y Orgánica, Facultad de Farmacia, (UGR), Centre for Genomics and Oncological Research, Pfizer/UGR/Andalusian Regional Goverment, PTS Granada, Granada, Spain
- 4. Laboratorio de estudios cristalográficos, Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR), Granada, Spain

email: gec@ugr.es

Novel bionanomaterials are hybrid materials that include the combination of biomolecules and inorganic substances to generate, enhance or support relevant properties. Bionanomaterials have useful applications in bio- and nanotechnology applications^{1,2} Among the biomolecules used to prepare hybrid materials, proteins have shown to be versatile materials thank to their capacity to self-assembly in crystalline form generating a porous network of nanometer size. The internal cavities of the protein have the ability to act as template^{3,4} and it gives the material the possibility to extrapolate nanoscale properties to macroscopic materials for practical applications.

In this work, we present a new methodology to homogenously incorporate inorganic particles within protein crystals using dipeptide hydrogels as growth media. To exemplify this methodology, we have obtained lysozyme crystals incorporating single wallet carbon nanotubes at different concentration. Crystals were grown in Fmoc-PhePhe-OH hydrogels³. The influence of the nanotubes on the diffraction properties, hardness, enzymatic activity and conductivity will be presented and discussed, as well as a full characterization of these new materials.

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Crystallographic and calorimetric studies with nuclear transport of DNA repair proteins

Marcos Roberto de Mattos Fontes¹, Andrea de Barros¹, Natalia Bernardes¹, Agnes Takeda¹, Thiago Dreyer¹, Maria Celia Bertolini², Bostjan Kobe³

- 1. Dept of Physics and Biophysics São Paulo State University (UNESP), Botucatu, Brazil
- 2. Dept of Biochemistry and Technological Chemistry São Paulo State University (UNESP), Araraquara, Brazil
- School of Chemistry and Molecular Biosciences, University of Queensland, Brisbane, Australia

email: fontes@ibb.unesp.br

The DNA damage can occur by several agents which may promote instability of the genome leading to several diseases such as cancer, neurological disorders, immunodeficiencies and premature aging. To avoid this serious consequences, cells have evolved a number of DNA repair pathways, which carry out the process in multiple steps to repair specific DNA damage, and maintain the integrity of the genome. The nuclear import is a pre requisite for the functions of DNA repair proteins and their correct location is essential. The classical nuclear import pathway is the best characterized and, probably the most used protein import mechanism to the cell nucleus, which involves the binding of the cargo protein via nuclear localization sequence (NLS) recognized by the importin-a protein (Impa). Classical nuclear localization sequences are targeting signals that link the cargo proteins to the Impa import receptor. They are formed by one or two basic clusters of amino acid residues, termed monopartite or bipartite NLSs. Aiming to understand the structural basis of the nuclear import process of DNA repair proteins, we have used X-ray crystallography and calorimetric tools to study the interaction between Impa and the NLS regions of each protein. Five different complexes have been studied, which cover the most important DNA mechanisms: i) base excision repair (BER) - FEN1 protein, ii) nucleotide excision repair (NER) - XPG protein, iii) mismatch repair (MMR) - PMS2/MLH1 heteodimer and iv) non-homologous end joining (NHEJ) - Ku70/Ku80 hetorodimer. We demonstrated that all these proteins are able to be transported to the cell nucleus by classical nuclear import pathway using monopartide or bipartite NLS sequences. However, we demonstrated that, for many of these proteins, the NLS regions are different from the previously described data in literature. In addition, new structural features related to minor and linker NLS binding regions were observed, which may give specificity for the transport of different DNA repair proteins.

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Keywords: importin-alpha, Nuclear transport, DNA repair proteins

MS04-P04

Structural characterization and comparison of crystallization behaviour of selected haloalkane dehalogenases

Ivana Kuta Smatanova¹, Tatyana Prudnikova¹, Radka Chaloupkova², Michal Kuty¹, Andrii Mazur¹, Barbora Kascakova¹, Jiri Damborsky², Pavlina Rezacova^{1,3}

- Institute of Chemistry and Biochemistry, Faculty of Science, University of South Bohemia Ceske Budejovice, Ceske Budejovice, Czech Republic
- Loschmidt Laboratories, Faculty of Science, Masaryk University Brno, Brno, Czech Republic
- Institute of Molecular Genetics AS CR Praha, Praha, Czech Republic

email: ivanaks@seznam.cz

Halogenated aliphatic compounds represent one of the largest groups of environmental pollutants. Haloalkane dehalogenases are responsible for one of the key reactions in the bacterial degradation of various halogenated pollutants. Apart from applications in bioremediation, haloalkane dehalogenases can be potentially applied in biosensing of pollution, biosynthesis, cellular imaging and protein immobilization. These enzymes catalyze the cleavage of a carbon-halogen bond in haloalkanes with water as the sole co-substrate, resulting in formation of a halide ion, a corresponding alcohol, and a proton. The role of conformational flexibility has been well established in connection with the accessibility of the active site, the binding of substrates and ligands, and release of products, stabilization and trapping of intermediates, orientation of the substrate into the binding cleft or adjustment of the reaction environment.

Several haloalkane dehalogenase structures were determined by X-ray diffraction analysis of enzymes' crystals, providing a good theoretical framework for their modification by protein engineering. Crystallization conditions for haloalkane dehalogenases DhaA from Rhodococcus rhodochrous NCIMB 13064, LinB from Sphingobium japonicum UT26, and DbeA from Bradyrhizobium elkanii USDA94 and their mutant variants were compared and analyzed. Analysis of crystallization cocktails revealed common components for the majority of compared dehalogenases such as divalent cations such as calcium or magnesium, and medium size polyethylene glycols (PEGs) 3350 or 4000 as well as almost neutral pH. Instead of X-ray diffraction analysis our model systems have been also investigated by other structural methods such as neutron crystallography, time-resolved crystallography and hydrogen-deuterium exchange mass spectrometry. Based on carefully designed experiments and by combination of the information obtained from different, but complementary, techniques we will be able to get inside into (i) conformational changes of selected enzymes upon their interactions with substrates, (ii) location of hydrogen atoms inside the enzyme active site and the access tunnels and (iii) protonation state of catalytic residues of the enzymes during their catalytic cycles.

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Keywords: haloalkane dehalogenases, crystallization, structure

Protein misfolding in chimeras of the sh3 domain of the c-src and fyn tyrosine kinase

Marina Plaza1, Ma Carmen Salinas-Garcia1, Ana Camara-Artigas1

 Department of Chemistry and Physics, CIAIMBITAL, University of Almería-ceiA3, Almería, Spain

email: mpg159@inlumine.ual.es

In the next few years, due to the increase in life expectancy, neurodegenerative diseases, as for example the Alzheimer's disease, will be one major health problem in the developed countries. This disease belongs to the group of those caused by protein misfolding associated with the development of amyloid deposit. The study of the molecular basis of the missfolding processes is complicate due to the difficulties to obtain structural information at atomic level of such class of oligomers. However some proteins suffer misfolding forming oligomers which are able to crystallize. This oligomerization process is known as 3D domain-swapping (3D-DS), and the interchage of secondary structure elements may result in the formation of dimers, trimers, etc1. A case of study is the SH3 domain of the c-Src tyrosine kinase which develop intertwined dimers and, also, is able to form amyloid fibers. The formation of these 3D-DS structures and amyloids is pH dependent and very responsive to some puntual mutations². Considering the results obtained in previous studies, our group have clonned, expressed and purified several chimeric proteins of the SH3 domain of the c-Src and Fyn tyrosine kinase, where the RT and n-Src loops of each domain have been interchanged3. In the c-Src SH3 the n-Src loop acts as hinge loop, which facilitate the opening of the domain to form the intertwined oligomer. We have study the stability of these proteins vs the pH (pH range 1-14) and in presence of the chemical denaturant guanidinium hydrochloride. These chimeric proteins are stable in a broad range of pH (pH 5.0-11.0) and show a high stability. The stability is higher at neutral pH than at acidic pH values. We have determined the oligomerization of the proteins by dynamic light scattering. The formation of dimers at acidic pHs is favoured by the addition of low molecular weight PEGs. Considering these results, we have screened the crystallization conditions at different pHs and in presence of several additives that promotes the formation of the dimers. Here we present the preliminary biophysical characterization of these chimeric proteins and their crystal structures determined at several pH values and oligomeric states. The results obtained show that besides residues at the hinge loops some residues al the distal loop might play a key role in the opening of the protomer to form the intertwined oligomers.

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Keywords: SH3 domain, domain swapping, misfolding

MS04-P06

Crystal structures of chimeric sh3 domains forming 3d-domain swapping in presence of urea

Mari Carmen Salinas-Garcia¹, Marina Plaza-Garrido¹, Ana Camara-Artigas¹

 Department of Chemistry and Physics, CIAIMBITAL, University of Almería-ceiA3, Almería, Spain

email: msg200@inlumine.ual.es

Amyloid forming proteins are the main cause of many neurodegenerative diseases. However, the mechanism of their formation at molecular level is not known. Tackling this task is difficult because the limitations to obtain high resolution structural information. We have constructed several chimeric proteins of the SH3 domains of the tyrosine kinases c-Src, Abl and Fyn as model proteins to tackle these studies. In those SH3 domains the RT and n-Src loops of each domain have been interchanged. Previous studies have demonstrated that some of these chimeric proteins are able to form oligomers by 3D domain-swapping (3D-DS), and the interchage of secondary structure elements results in the formation of dimers^{1,2}. Structural studies performed with proteins under conditions near denaturation might help to understand the initial steps which drives misfolding in proteins. Considering this approach, we have studied the binding of the chemical denaturant urea to several chimeric constructions of the c-Src SH3 domain. We have crystallized these proteins in presence of different concentrations of urea to determine its interaction. Previously, we have analyzed the unfolding of the chimeric proteins in presence of urea at pH 5.0 and pH 7.0 by means of the intrinsic fluorescence of the protein. Some chimeras of the Src-SH3 where the RT and n-Src loops have been interchanged by those present in the Fyn SH3 domain (SF chimeras) does not fit a two-state model, which might indicate the presence of some intermediate in the unfolding process as it has been described in other SH3 domains³. Most of the crystals grown in presence of urea diffracted to atomic resolution, which allowed us to model the urea molecules interacting with residues at the surface of the protein. In all the structures solved the urea molecules were modelled replacing first-shell water molecules, which would modify the water-water hydrogen bond network. We have analyzed the results considering structural changes due to urea binding: in the position of the protein main chain; rotamer side chain changes; and, displacement of buried water molecules. In some structures a urea molecule is placed interacting with Glu106, which is critical in the nucleation of the folding process of the c-Src-SH3 domain by forming a hydrogen bond with Ser123.

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Keywords: 3-D domain swapping, SH3-domain, Unfolding

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Structural basis for transcriptional control of flagellum assembly by the FliD-FliT complex

Hyung Ho Lee

1. Department of Chemistry, Seoul National University, Seoul, Korea South

email: lee.hyungho@gmail.com

During the stages of the flagellar assembly process, the flagellar genes are expressed in response to morphological development of flagellar assembly. Flagellar biogenesis is controlled by a negative feedback loop. When FliD was secreted at the late step of flagellar assembly, the FliD-FliT complex disassembled and free FliT bound to the FlhDC complex, a master regulator of flagellar biogenesis, subsequently inhibiting the overall expression of flagellar proteins. Thus, the overall production of flagellar proteins is reduced by sensing flagellar morphology via FliD-FliT complex. In this study, we analyzed the role of the FliD C-terminal domain in pentamer formation and interaction with FliT. We determined the crystal structure of C-terminal domain of FliD bound to FliT, and showed that the FliD Leu443, which is part of the hydrophobic core of the FliD-FliT complex, plays a crucial role in the pentameric oligomerization of FliD. When the FliD Leu443 was mutated, the binding affinity between FliD and FliT was significantly reduced, and it exists as a monomer in solution. Consistently, lengths of flagella in each cell were significantly reduced in L443R mutant strain, suggesting that normal flagellar biogenesis was impeded. These results suggest that the C-terminal domain of FliD plays a crucial role in the pentameric oligmerization of FliD and the binding of FliT to the C-terminal domain of FliD is critical to inhibit the premature assembly of the FliD pentamer in the cytosol.

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Keywords: Flagellum, FliD, FliT

MS04-P08

Liquid Dense Clusters: Intermediates between Nanocrystals and Single Particles

Hevila Brognaro¹, Sven Falke², Robin Schubert², Christian Betzel ²

- Center for Free Electron Laser Science. Deutsches Elektronen-Synchrotron (DESY)., Hamburg, Germany
- Laboratory for Structural Biology of Infection and Inflammation, c/o DESY, Institute for Biochemistry and Molecular Biology, University of Hamburg, Hamburg, Germany

email: hevila.brognaro@desy.de

Liquid-dense clusters (LDCs) are formed by liquid-liquid phase separation, which is a process known for a long time *in vitro* as well as *in vivo* affecting a variety of nucleic acids, protein functions and metabolic pathways. Insights in the formation and dynamics of liquid dense clusters will open also new option to optimize protein crystal growth [1].

Nonetheless, the knowledge about structural and dynamic properties of macromolecule LDCs of proteins and different nucleic acids remains by far incomplete (1). Insights about the folding state and packing of biomolecules inside LDCs will aid in understanding the relevance of metastable liquid-liquid phase separation, as well as understanding initial processes of protein aggregation, oligomerization and misfolding, e.g. in neurodegenerative diseases like Alzheimer, Parkinson, dementia and sclerosis [2]. In order to investigate formation and internal structure of liquid dense clusters (LDC) by coherent X-ray diffractive imaging, selected distinct proteins of high medical and biological relevance as well as RNAs were selected to prepare LDCs. The physico-chemical conditions for the formation, stabilization and labelling of selected macromolecule LDCs were established and systematically optimized. The influence of polyvalent ions and polyethylene glycols as precipitant agents, which can promote LDC formation, were investigated. A combination of single particle Brownian microscopy applying an ultrafast camera, in situ Dynamic Light Scattering as well as fluorescens and atomic force microscopy have been applied to follow the time resolved process of clusters formation. Initial results and data obtained were utilized to understand and to optimize the clusters formation, as well as assess their stability, also towards advanced X-ray imaging techniques. More detailed information about folding state and arrangement of macromolecules inside LDCs, particularly by using X-ray free electron laser based imaging will open new routes to utilize LDCs for structural investigation of nanomaterials and single macromolecules in a non-crystalline environment in the future, and will allow to prepare distinct nano- and micro-sized crystals, most suitable for serial diffraction data collection. Details will be presented.

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Keywords: liquid dense clusters, crystal nucleation

Incorporation of an unnatural amino acid as IR sensor for conformation-specific detection of calmodulin-binding

Anne Creon¹

 Department of Chemistry, Institute of Biochemistry and Molecular Biology, Hamburg, Germany

email: anne.creon@chemie.uni-hamburg.de

Here we present the use of an unnatural amino acid as IR sensor for conformation-specific detection of calmodulin-binding. Calmodulin (CaM) is an eucaryotic protein that binds four Ca²⁺ ions and acts as a calcium sensor by translating the Ca²⁺ signal into cellular processes. The binding of calcium leads to conformational changes of CaM which enable Ca²⁺/CaM to recognize and bind various target proteins. There are diverse binding partners and binding modes of CaM. For the conformation-specific detection of the CaM-binding to its partner, we incorporated the unnatural amino acid *p*-azidophenylalanine (AzF) in different positions of calmodulin.

AzF contains the azide vibrational reporter that shows a characteristic IR signal in a defined region of the infrared spectrum where the native protein does not display any IR-signals. The unnatural amino acid can be used to detect changes in the chemical environment. We followed the signal of the AzF probe in various CaM/peptide-complexes by FTIR spectroscopy. This system allows conformation-specific detection of CaM binding to its binding partners. With the crystallization of the CaM/peptide-complexes we want to get more insight into the structures with the incorporated unnatural amino acid.

Keywords: unnatural amino acid, calmodulin, IR spectroscopy

MS04-P10

The Durham Screens: Fast Protein Buffer Optimisation through Differential Scanning Fluorimetry

Dan Bruce1, Ehmke Pohl1

1. Department of Biosciences, Durham University, Durham, United Kingdom

email: daniel.bruce@durham.ac.uk

Modern crystallographers are capable of unprecedented speed and throughput in their work, from target purification and crystallisation to diffraction data acquisition and analysis. Protein stability is a key factor in the crystallisation process; samples must be conformationally homogenous and structurally sound over a period of days to form high-quality diffracting crystals. We present The Durham Screens, a set of three complimentary 96-condition screens designed to efficiently identify conditions favourable to protein stability.

Differential Scanning Fluorimetry (DSF, also known as Thermofluor and the Thermal Shift Assay) has rapidly become the go-to method for protein stability analysis due to its high throughput, low cost and versatility. By monitoring the thermal denaturation of a protein sample using either its intrinsic fluorescence or an environmentally-sensitive fluorescent dye, DSF can compare a range of conditions and identify those that confer the greatest thermal stability.

The Durham Screens are designed around three themes: pH, salts and osmolytes. By deconvoluting the contributions of each buffer component to the overall stability of a protein sample, the screens provide valuable insights to optimise purification protocols, protect stored samples and guide rationally-designed crystallisation trials.

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Keywords: Sample optimisation, DSF

Size exclusion chromatography as a labbased indicative for protein self-assembly prior to nucleation

Alaa Adawy1, Matthew Groves2

- Laboratory of High-Resolution Transmission Electron Microscopy, Scientific-Technical Services, University of Oviedo-CINN, Oviedo, Spain
- Department of Drug Design, Structural Biology Unit, Groningen Research Institute of Pharmacy, University of Groningen, Groningen, Netherlands (Holland, Europe)

email: hassanalaa@uniovi.es

The potential use of size exclusion chromatography (SEC) as a lab-based scanning methodology to monitor protein self-assembly prior to nucleation is the subject of this study. The effect of the mobile phase ionic strength and protein concentration on the output of SEC experiments was exploerd using high-resolution size exclusion chromatography (SEC) coupled with static light scattering (SLS) analyses. SLS is capable of monitoring abrupt changes in the molar masses and the results highlight the effect of small changes in the mobile phase composition on the estimation of molar masses calculated from retention time-based calibration curve compared with those obtained from SLS analysis. By comparing the SLS data with the SEC chromatograms, we show that SEC can provide helpful information on the protein aggregation state as macromolecules approach known precipitation points in their phase diagrams. This study implies that SEC can be usefully used to study phase diagrams of different proteins.



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Keywords: size exclusion chromatography, static light scattering, protein nucleation

MS04-P12

Site-Specific Analysis of UL144 Protein from Human Cytomegalovirus Highlights its Role in Virus-Mediated Immune Evasion

Ivana Nemčovičová1, Mário Benko1, Marek Nemčovič2

- Department of Viral Immunology, Biomedical Research Center, Slovak Academy of Sciences, Bratislava, Slovakia
- 2. Department of Glycobiology, Institute of Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia

email: viruivka@savba.sk

Human cytomegalovirus (HCMV, HHV-5) causes a spectrum of disease syndromes in children and adults. HCMV is a cause of mononucleosis in immunocompetent individuals and is a well-known cause of serious morbidity and sometimes fatal infections in immunocompromised patients, especially recipients of solid-organ or hematopoetic cell allografts and individuals with advanced AIDS. HCMV molds cell functions to support its replication and displays tropism for differentiated human cells that are critical for its life cycle. HCMV destroys infected cells by active lytic replication. The virus genes block apoptosis, interfere with the expression of immune recognition molecules on the surface of infected cells to avoid lysis by natural killer or cytotoxic T cells, and inhibit the antiviral effects [1]. The large size of the HCMV dsDNA genome, allows this virus to dedicate many genes to viral fitness; a number of these genes thwart the host inflammatory, innate, and adaptive immune responses. In clinical HCMV isolates, considerable genetic polymorphism exists and correlates with its clinical presentation. Of the viral genes, UL144 is particularly notable because of its role in modulating the host immune response. UL144 is found exclusively in clinical HCMV strains and encodes a structural homologue of the herpesvirus entry mediator. It has been proposed that UL144 plays a role in virus-mediated immune evasion by transmitting inhibitory signals to downregulate T-cell responses [2].

Sequence of HCMV UL144 shows 10 N-linked glycosylation sites located in extracellular part of the gene. Many of them are not present in other viral species that suggest that potential glycosylation is important only in humans and may play a role in ligand-binding recognition. Here, we present the characterization of such recombinant HCMV UL144 glycoprotein isolated from baculovirus-insect system. By liquid chromatography-tandem mass spectrometry (LC-MS/MS) we have identified up to 6 peptides of HCMV UL144 genes that have covered the most of the desired sequence. Intact protein analysis using a combination of LC and MS determined the accurate masses of these proteins (glycan-deficient mutein and native wild-type) and the relative abundance of their isoforms. We have also analyzed the glycan profiles and identified the most glycosylated UL144 species that showed mass of 20267,4 Da. As glycosylation plays an important role in receptor-ligand recognition we have performed the SPR binding studies to UL144 known cellular ligands that have show the importance of UL144 glycosylation in HCMV immune recognition.

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Keywords: immunomodulation, HCMV UL144, glycosylation

MS04-P13

Structure-based cofactor binding properties of dihydrodipicolinate reductase (PaDHDPR) from Panisporosarcina sp. TG-14

Chang Woo Lee1, Jun Hyuck Lee2, Sun-Ha Park3

- 1. Polar Science, University of Science and Technology, Incheon, Korea South
- 2. Unit of Polar Genomics, Korea Polar Research Institute, Daejeon, Korea South
- 3. Unit of Polar Genomics, Korea Polar Research Institute, Incheon, Korea South

email: justay@kopri.re.kr

Dihydrodipicolinate reductase (DHDPR) is a key enzyme for the Diaminopimelate (DAP) and Lysine synthesis pathway by reducing the dihydrodipicolinate (DHDP) into tetrahydrodipicolinate (THDP) using NAD(P)H as a cofactor. It is known that DHDPR uses both NADPH and/or NADH as cofactor but the structural basis of its cofactor specificity is still unclear. In this study, we found that PaDHDPR from Paenisporosarcina sp. TG-14 has a strong preference for NADPH compared with NADH based on isothermal titration calorimetry and enzyme activity assay. To better understand the enzymatic mechanism of PaDHDPR in molecular level, the three crystal structures of unliganded, DPA (dipicolinate; a competitive inhibitor of DHDPR) bound and ternary (NADPH and DPA) complexed PaDHDPR were determined at 1.8, 1.8 and 2.1 Å resolutions, respectively. Comparison of these PaDHDPR structures with previously reported other DHDPR structures reveals that only ternary complex PaDHDPR structure shows completely closed conformation suggesting both substrate and nucleotide co-factor are essential for the domain movement. Moreover, NADPH binding induced local conformation changes in the N-terminal long loop region (residues 34-59) in PaDHD-PR and the His35 and Lys36 residues located in this loop region make strong interaction network with the 2'-phosphate group of NADPH. These specific interactions may allow PaDHDPR to have a strong preference to NADPH as co-factor compared with NADH. In addition, activity assay using H35A and K36A mutants showed significantly reduced NADPH binding and enzymatic activity confirming the importance of these two residues. Collectively, these data provide detailed structural insights into pivotal conformational changes in PaDHDPR for enzymatic catalysis and the cofactor selectivity of this important bacterial enzyme.

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Keywords: dihydrodipicolinate reductase, Panisporosarcina sp. TG-14, psychrophile

MS05 - Structural information in drug design

Chairs: Dr. Rob van Montford, Prof. Andreas Heine

MS05-P01

Crystal structure and vibrational study of diphenylhydrazine dihydrogenophosphate monocrystal DPHDP $(C_6H_9N_2)_2H_2P_{2\&l}$

Soufiane Zerraf¹, Mustafa Belhabra¹, Aziz Kheireddine², Malika Tridane³, Said Belaaouad¹

- Laboratory of Physical Chemistry of Materials LCPM, Faculty of Sciences Ben M'sik, B.P. 7955. Bd Cdt Driss El Harti. Hassan II University of Casablanca. Morocco, Casablanca, Morocco
- Laboratory of Physical Chemistry of Materials LCPM, Faculty of Sciences Ben M'sik, B.P. 7955. Bd Cdt Driss El Harti. Hassan II University of Casablanca. Morocco, Casablanca, Morocco
- Regional Center for Education and Training Occupations Casablanca Anfa, Bd Bir Anzarane Casablanca. Morocco., Casablanca, Morocco

email: soufiane.zerraf@gmail.com

Chemical preparation, crystal structure and vibrational study are reported for a new diphenvlhydrazine dihydrogenophosphate monocrystal DPHDP (C6H9N2)2H2P2O7 . This organic cationic diphosphate (C6H9N2)2H2P2O7 was synthesized by the method of ion exchange resin. $(C_6H_9N_2)_2H_2P_2O_7$ crystallizes in the monoclinic system, with a merit factor of 0.0285, space group $P2_1/c$, a = 7,1991 (2) Å, b = 8,0209 (4) Å, c =31,2070(2) Å, β = 93,577(1)°, Z = 4, V = 1798.5 (1) Å^{3.} The crystal structure was refined down to R = 0.027, R =0.069 for 1830 reflections satisfying criterion I $\ge 2\sigma$ (I). The structural resolution shows the existence of $H_2P_2O_7^2$ ion chains linked together by hydrogen bonds. The organic cations C6H9N2+ and the phosphate chains are linked together by hydrogen bonds. Diphosphate group adopt an eclipsed configuration. A network of O-H... O hydrogen bonds reinforce the cohesion of the structure. The vibrational study by IR absorption spectroscopy of the title compound reveals the presence of three bands and confirms the existence of non-equivalent positions of water molecules in the structure.

 $(C_6H_9N_2)_2H_2P_2O_7$ is a non linear optical NLO product as it is not centrosymetric.

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Keywords: Crystal structure, vibrational study, X-ray diffraction.

MS05-P02

Chemical preparations, crystal data and vibration Spectroscopic Study of single crystal L-arginine phosphate monohydrate

Hamza Marouani¹, Soufiane Zerraf¹, Mustafa Belhabra¹, Aziz Kheireddine¹, Malika Tridane², Said Belaaouad¹

- Laboratory physico-chemical materials science faculty ben m'sik univérsité hassan 2 department of chemistry, Casablanca, Morocco
- Regional Center for Education and Training Occupations Casablanca Anfa, Bd Bir Anzarane Casablanca, Casablanca, Morocco

email: marouanihamza7@gmail.com

A single-crystal was selected from the reaction product of a stoichiometric mixture of phosphoric acid (H₃PO₄) to which was added the Arginine (C₆H₁₄N₄O₂) and its crystal structure determined from three-dimensional X-ray diffraction data. The structure is monoclinic, space group P2, a=7.3450(14) Å, b=7.9176(15) Å, c=10.8796(22) Å, β =97.98(2)°, V=626.57(186) Å³ and Z=2, least squares refinement was converged to R1=0.0456, wR2=0.1433 for 3278 unique reflections. The structure consists of chains formed by edge sharing of PO4 tetrahedra, water and arginine. The stacking along b axis consists of these chains bridged by layers formed by PO4 water and arginine by hydrogen bonds. The Raman and infrared spectra of single crystal LAP were recorded to determine the symmetries of the vibrations of the various molecular groups such as NH₂⁺, NH₂, CH₂, CH, COO⁻, H₂O and H₂PO₄ present in the crystal.



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Keywords: Chemical preparation, infrared vibration spectrometry, X-ray diffraction.

The Crystal Structure of the R280K Mutant of Human p53 Explains the Loss of DNA Binding

Ana Luisa Carvalho¹, Ana Sara Gomes², Filipa Trovão¹, Benedita Pinheiro¹, Sara Gomes², Carla Oliveira³, Lucília Domingues³, Maria João Romão¹, Lucília Saraiva²

- Ucibio-Requimte, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Caparica, Portugal
- Laqv-Requimte, Laboratório de Microbiologia, Departamento de Ciências Biológicas, Faculdade de Farmácia, Universidade do Porto, Porto, Portugal
- 3. CEB—Centre of Biological Engineering, University of Minho, Campus Gualtar, Braga, Portugal

email: almc@fct.unl.pt

The p53 tumor suppressor is widely found to be mutated in human cancer. This protein is regarded as a molecular hub regulating dilerent cell responses, namely cell death. Compelling data have demonstrated that the impairment of p53 activity correlates with tumor development and maintenance [1]. For these reasons, the reactivation of p53 function is regarded as a promising strategy to halt cancer [2]. The recombinant mutant p53R280K DNA binding domain (DBD) was produced for the "rst time, and its crystal structure was determined in the absence of DNA to a resolution of 2.0 Å [3]. The solved structure contains four molecules in the asymmetric unit, four zinc(II) ions, and 336 water molecules. The structure was compared with the wild-type p53 DBD structure, isolated and in complex with DNA. These comparisons contributed to a deeper understanding of the mutant p53R280K structure, as well as the loss of DNA binding related to halted transcriptional activity. The structural information derived may contribute to the rational design of mutant p53 reactivating molecules with potential application in cancer treatment.

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Keywords: mutant p53R280K, crystal structure, DNA binding

Co-crystal forms of the BCS class IV drug sulfamethoxazole

Moneerh Alsubaie¹, Marwah Aljohani¹, Andrea Erxleben¹, Patrick McArdle¹

1. School of Chemistry, National University of Ireland Galway, Galway, Ireland

email: m.alsubaie1@nuigalway.ie

Sulfamethoxazole, smz, is an antibiotic which is classified as a Biopharmaceutics Classification System (BCS) class IV, low solubility and low permeability drug. Co-crystal formation has been examined in an attempt to improve solubility. Both ball milling and crystallization from solution have been examined. Ball milling showed that thirteen co-formers gave new crystalline X-ray powder patterns and four gave X-ray amorphous patterns while crystallization from solution gave single crystals of four co-crystals and a salt. The co-formers which gave the co-crystals and the salt have better H-bond acceptors than the sulfonyl oxygens of smz. The 4,4-dipyridyl co-crystal has an interesting high Z" structure. It crystallized in space group P1 with four smz and six 4,4'-dipyridyl molecules in the asymmetric unit. The lattice energies of smz and the co-crystals were estimated using the PIXEL program. The dissolution rates of the co-crystals are all lower than smz form I despite the fact that they have lower computed lattice energies than smz form I. It appears that the absence of any hydrogen bond in the smz form I structure with a D...A distance less than 3.2 Å and the presence of stronger hydrogen bonds in the co-crystals with D...A distances close to 2.8 Å is more important in determining dissolution rates than lattice energies.

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Keywords: Cocrystal

MS05-P05

Co-crystals of fenamic acids with ethacridine

Marta Krawczyk1, Sara Głód1, Irena Majerz1, Monika K. Krawczyk2

- 1. Department of Analytical Chemistry, Faculty of Pharmacy, Wrocław Medical University, Wrocław, Poland
- Institute of Experimental Physics, University of Wrocław, M. Borna 9, 50-204, Wrocław, Poland

email: martakrawczyk.re@gmail.com

It is expected that co-crystals of drug substances with different pharmaceutical properties and medical activities will be characterized by a wider spectrum of activity, new therapeutic properties and better bioavailability of the drug [1].

Although fenamic acids are very popular non-steroidal anti-inflammatory substances [2] used in therapy, their physical properties as solubility in water connected to the pharmaceutical dosage needs to be improved.

Ethacridine lactate is a drug used as an antiseptic agent therefore it can be expected that co-crystals of ethacridine with fenamic acids will combine pharmaceutical properties of both components and additionally will be characterized by improved bioavailability.

Organic complexes of fenamic acids (fenamic, mefenamic, flufenamic, tolfenamic)

and ethacridine have been obtained by formation of the network of intermolecular of N–H···O and C–H···O hydrogen bonds, occurring between the components of the co-crystal, as well as O–H···O and N–H···O hydrogen bonds generated by fenamate and ethacridine species along with water molecules. The crystal structure of fenamic acids with ethacridine will be presented and analysis of the hydrogen bonds will be performed.

Finacial support: Grant of the Wrocław Medical University STM.D050.17.002.

Figure. Structure of co-crystal of mefenamic acid with ethacridine.



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Keywords: fenamic acids, co-crystal, ethacridine

Stability of API. Lactamization of γ-amino acids in crystal state

Marek Glowka1, Waldemar Maniukiewicz1

1. Faculty of Chemistry, Lodz, Poland

email: marek.glowka@p.lodz.pl

γ-Aminobutyric acid (GABA) plays numerous physiological functions and its derivatives are potential active pharmaceutical ingredients (API). At the moment two of them (Baclofen and Gabapentin – see below) are widely used. **Baclofen** (Kemstro, Lioresal) is an agonist of GABA receptors. It shows significant muscle relaxant activity and is used as antispastic drug while **Gabapentin** (Prebalin, Lyrica) shows anticonvulsant activity and is used mainly as antileptic drug, in neurophatic pain and in generalized anxiety disorder.

GABA and its neutral derivatives exist in a dipolar (zwitterionic) form both in solid states and in solutions (see below), which theoretically should prevent possible nucleophilic attack of the electron lone pair at N atom (engaged in N-H bond in protonated forms) on the carboxylic carbon (only in neutral carboxylic group) with formation either cyclic x-lactam or linear peptide. The reaction is observed quite often in solutions, where a tiny concentration of the neutral form of the amino acids being in equilibrium with the ionic forms allows such reaction to go. The reaction (shown below) was also observed in the solid state by Borka [1] in the case of Baclofen at elevated temperatures. Surprisingly, one of several solid Baclofen forms under study in our laboratory revealed the lactamization reaction in moderate temperatures.

The analysis of crystal structures of γ -amino acids found in Cambridge Structural Database and in our archives (unpublished ones) allowed us to point out several factors, which have to be taken into account when considering perspective stability of such API.

The most important features are:

- · conformation of the main amino acid chain,
- shortest intra- and intermolecular distances between amino and carboxyl groups,
- geometry and strength hydrogen bonds formed by the two reacting groups,
- · relative spatial orientation of the two groups,
- possibility of rotation of the carboxyl group.

The common values of the analyzed factors and their inluence on lactamization of x-amino acid will be presented.



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Keywords: GABA derivatives, Lactamization in crystals, API stability

MS05-P07

Fragment screening on protein Kinase A and PIM1-Kinase

Andreas Heine¹, Christof Siefker¹, Gerhard Klebe¹

1. Institute of Pharmaceutical Chemistry, Philipps-University Marburg, Marburg, Germany

email: heinea@mailer.uni-marburg.de

Fragment screening is a method routinely applied in pharmaceutical drug development by now. Here, small molecules (<300 Da) that are identified during the screening process are developed into lead compounds with high affinity. While high-throughput screening usually requires large compound libraries, fragment libraries can be much smaller in size, containing only several hundred to thousand molecules. We developed a small fragment library composed of 361 compounds and validated it on the aspartyl protease endothiapepsin for which we obtained a high hit rate during crystallographic screening.[1,2]

We used this library to screen protein kinase A (PKA) and PIM1-kinase. For pre-screening we applied a thermal shift assay (TSA) to identify suitable fragments for crystallographic screening. In the TSA 31 fragments were identified for PKA and 52 for PIM1. These fragments were then subjected to crystallographic screening where we obtained 15 complex structures for PKA and 13 for PIM1, indicating also here a high crystallographic hit rate. In comparison we tested a random collection of fragments for crystallographic screening with PKA resulting in a much lower hit rate (21%). Deviating hit lists in the TSA assay and only one common fragment observed in both kinase structures suggest that fragments might be selective binders. TSA screening results, observed binding motifs and structural differences in the ATP-binding pockets of both kinases will be discussed in detail.

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Keywords: fragment library validation, structure-based drug design, crystallographic fragment screening

Mechanistic study of human phosphoserine phosphatase (hPSP) via crystallization with intermediates

Marie Haufroid1-2, Manon Mirgaux1-2, Johan Wouters1-2

- 1. Laboratoire de Chimie Biologique Structurale (CBS), Université de Namur (UNamur)
- Namur Medicine & Drug Innovation Center (NAMEDIC-NARILIS) Namur, Belgium

email: marie.haufroid@unamur.be

Human phosphoserine phosphatase (hPSP) catalyses the third and final step of the serine pathway, which is the transformation of O-Phospho-L-Serine into L-Serine. This Mg²⁺ enzyme is part of the Haloacid Dehalogenase superfamily of enzymes and possesses a Rossman-like domain in order to orient the substrate within the active site. This protein is also a therapeutic target in colorectal cancer [1]

In this work, hPSP was produced, purified and crystallized in various conditions. In order to design inhibitors and gain a better understanding of the catalytic mechanism, we co-crystallized the enzyme in presence of different substrates and inhibitors. Crystals were obtained and data were collected at SOLELL Synchrotron in France.

After resolution, we obtained a co-crystal of hPSP with phosphate as a ligand at a resolution of 1.5 Å. We also resolved a dynamic loop that was absent in the other high-resolution structure of hPSP (PDB: 1NNL) [2]. This loop was also described by Kim *et al* with a resolution range going from 2.5 to 2.8 Å but was placed in a different manner (PDB: 1L8L & 1L8O) [3]. The dynamic properties of this chain indicates a possible induced fit in order to open and close the active site during reaction.

We will complete those results thanks to other co-crystallization assays of hPSP with ligands. Moreover, we will apply dynamic simulations to elucidate the catalytic mechanism of this enzyme.

Acknowledgment. The authors thank members of namedic who generated namedic library used for inhibition and crystallization assays, in particular Prof B. Masereel and L. Pochet. Authors also acknowledge SOLEIL for provision of synchrotron radiation facilities and we would like to thank Leonard Chavas for assistance in using beamline Proxima I.

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Keywords: Phosphoserine phosphatase, protein crystallization, co-crystallization

MS05-P09

Structural investigation of the interaction between Combretastatin A-4 analogues with benzoxazolone scaffold and αβtubulin

Rusi Rusev¹, Mariana Gerova², Georgi Atanasov³, Desislava Stanisheva², Hristina Sbirkova-Dimitrova⁴, Margarita Apostolova³, Ognyan Petrov², Boris Shivachev⁴

- Institute of mineralogy and crystallography -Bulgarian academy of sciences, Sofia, Bulgaria
- 2. Faculty of chemistry and pharmacy, Sofia University, Sofia, Bulgaria
- 3. Institute of Molecular Biology "Acad. R. Tsanev", Bulgarian Academy of Sciences, Sofia, Bulgaria
- Institute of Mineralogy and Crystallography "Acad. Iv. Kostov", Bulgarian Academy of Sciences, Sofia, Bulgaria

email: r.rusev93@gmail.com

A series of 70 new Combretastatin A-4 (CA4) analogues have been synthesized by modified Wittig reaction [1]. The compounds were tested in vitro for cell growth inhibition and the ability to induce apoptosis against HepG2, EA.hy926 and K562 cell line. The most active compounds were further tested against HT-29, Colon-26, A-549, MCF-7, MDA-MD-231, MCF-10A, HaCaT and NHEK lines. The new compounds have been characterized by single crystal diffraction and preliminary data about the interaction of the most active CA-4 analogues has been obtained using fluorescence displacement assay. The crystallization of selected analogues with $\alpha\beta$ -tubulin-RSB complex suggested that interaction might occur at different sites though the "small molecules" are structurally very alike (Fig. 1). Figure 1. General scheme of synthesized analogues a), ORTEP view of the molecule of compound SZ16 present in the asymmetric unit [1] b) and possible interaction (binding) sites of the analogues with $\alpha\beta$ -tubulin dimmer.

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Keywords: Stilbene, Tubulin binding, Anticancer agents

Towards understanding phase transitions of confined pharmaceuticals

Alexander Morritt¹, Karol Nartowski², László Fábián¹, Yaroslav Khimyak¹

- 1. School of Pharmacy, University of East Anglia, Norwich, United Kingdom
- 2. Wrocław Medical University, Wrocław, Poland

email: a.morritt@uea.ac.uk

The change in the phases of matter has been extensively studied; from simplistic thermal changes of liquids, solids and gases to more the complex transitions of the different forms of the same material. This is important for pharmaceuticals because different polymorphs of the same drug having different intrinsic properties such as solubility and bioavailability. In studying these systems it is difficult to isolate different phases of matter in the early stages of crystallisation, as when these transitional phases occur they have a limited lifetime. Therefore stopping/slowing microscale crystallisation in order to observe the early stages is the aim of this project. This is achieved by encapsulating the pharmaceutical into a host with confined nanoscale geometry, in this case a mesoporous silica host. This allows for an indirect route into understanding relationships between different phases and motilities of pharmaceutical materials. Melt loading methods were used to in order to encapsulate the cocrystal of flufenamic acid and nicotinamide (FFA/ NA) within the pores. Confirmation of loading at different ratios inside the pore was completed using DSC, nitrogen desorption isotherms. Subsequent NMR analysis was completed by solid state NMR methods to investigate the 1H, 13C and 19F environments by different correlation experiments under MAS conditions. Defined separate phase peaks using ¹⁹F NMR were observed previously in this material; surface, crystalline and amorphous peaks. Using 19F-19F NOESY NMR, interactions between these peaks were observed giving two out of the possible three interactions giving insight into spatial differences between the different phases of material.



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Keywords: phase, NMR, pharmaceuticals

MS05-P11

Novel fluorescent probes for retinoic acid binding proteins

Charles Tomlinson¹, Ehmke Pohl¹, David Chisholm¹, Andy Whiting¹

1. Department of Chemistry, Durham University, Durham, United Kingdom

email: c.w.e.tomlinson@durham.ac.uk

Development of new, fluorescent, retinoic acid analogues offers the opportunity to investigate retinoic acid binding proteins both in vitro and in vivo. Retinoic acid signaling is vital for normal growth and development, and offers an attractive target for novel therapies, particularly within the field of neurodegenerative disease. Through different binding affinities the capability of, and variation between, different protein isoforms can be investigated, and potentially harnessed to design isoform-specific ligands. The fluorescent nature of the probes, and their enhanced stability over that of retinoic acid, makes them ideal for following in vitro via fluorescence spectroscopy and will be invaluable for high throughput ligand screening - feeding into the structure based design of future ligands.

Keywords: Retinoids, Binding, Fluoresence

Structure-assisted design of Carborane inhibitors of human Carbonic Anhydrase IX

Pavlina Rezacova¹, Michael Kugler¹, Jiri Brynda², Bohumir Gruner³, Marián Hajduch⁴, Jan Nekvinda³, Klara Pospisilova¹, Viswanath Das⁴, Josef Holub³

- Institute of Organic Chemistry and Biochemistry, Czech Academy od Sciences, Prague, Czech Republic
- Institute of Molecular Genetics, Czech Academy od Sciences, Prague, Czech Republic
- Institute of Inorganic Chemistry, Czech Academy of Sciences, Rez, Czech Republic
- Institute of Molecular and Translational Medicine, Olomouc, Czech Republic

email: rezacova@img.cas.cz

Carbonic anhydrases (CAs) are zinc metalloenzymes playing an important role in many physiological processes. Several CAs are also involved in various pathological processes in humans and represent thus targets for drug development. Specifically, human carbonic Anhydrase IX (CA IX), isoform overexpressed in solid hypoxic tumours, is a target for cancer therapy and diagnostics. We have previously identified carboranes as a promising class of specific inhibitors of CA IX [1]. Here we report recent advances in the structure-assisted design of carborane and metallacarborane inhibitors targeting CA IX. We chose carboranes, three-dimensional scaffolds, which act as as space-filling fragments. We modified boron cages to synthetize carboranes and metallacarboranes substituted by sulfamide, sulfonamide or sulfamate groups, i.e. functions known to bind tightly to the zinc atom in the active site of CAs. Consequently, the small library of ca. 70 substituted carboranes and metallacarboranes was. Several compounds exhibit selective inhibitory activity toward CAIX with Ki values in low nanomolar or even picomolar range. Selected inhibitors were tested for their effect on tumor growth in BALB/c mice orthotopically implanted with 4T1 cells and SCID mice subcutaneous transplanted with HT-29 cells.

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Keywords: Anti-tumor agents, carborane inhibitors, Carbonic anhydrase IX

MS05-P13

VHHs as tools in antibody assisted structure based drug discovery

Sura Abbood¹

 Molecular and Cell Biology/ Leicester university, Leicester, United Kingdom)

email: sma43@leicester.ac.uk

Cytokines such as interleukin-6 (IL6) are attractive therapeutic targets in inflammatory diseases. Interleukin-6 is a secreted cytokine, produced by different cell types, but it originates mainly from macrophages and monocytes at the site of inflammation [1]. IL6 is a multifunctional cytokine and mediates its biological function via a hexameric signaling complex composed of two molecules each of IL6, gp80 and gp130 [2]. It is a key player in immunological response and has been implicated in the pathogenesis of a wide range of inflammatory diseases such as rheumatoid arthritis [3]. Heavy chain only antibodies are produced by the immune system of a limited number of animals, including camels and llamas and due to their small size are an attractive tool for antibody based drug discovery. A number of antigen-binding domain (VHH) antibodies that target IL6 have developed to inhibit the hexameric signaling complex formation. VHH94 was derived from a camel heavy chain antibody isolated after immunization with a interleukin-6-gp80 fusion protein. VHH94 was found to enhance the binding of IL-6 to gp80 potentially through binding to an allosteric site on IL-6 and partially inhibited the signaling of IL6. The combination of X-ray crystallography and NMR spectroscopy are using to provide a clear overall picture of the IL6-VHH94 interaction site.

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Keywords: IL-6, VHH94, Structure

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Galectin-3: studying role of fluorines in the protein-ligand interaction to achieve high affinity and selectivity

Rohit kumar¹, Kristoffer Peterson², Ulf Nilsson², Derek Logan¹

- 1. Biochemistry and Structural Biology, Lund university, Lund, Sweden
- 2. CAS, Lund University, Lund, Sweden

email: rohit.kumar@biochemistry.lu.se

Galectin-3 belongs to the galectin family that recognizes carbohydrates. It has a highly conserved carbohydrate recognition domain (CRD) of 130 residues, which is responsible for binding to beta-galactosides. Galectin-3 has been shown to be involved in cancer, angiogenesis and stroke. Its involvement in these important diseases makes it a wonderful drug target. Our previous work¹ showed the mode of binding of lactose and role of structured water molecules in carbohydrate binding site. These results prompted us to explore the molecular recognition and role of water molecules in designing high affinity inhibitors. Natural ligands of galectin-3 almost always have a galactose residue.

Selective small molecule galectin-3 inhibitors are valuable both as research tools to study protein-ligand interactions and as lead compounds in drug discovery. These compounds usually involve galactose-based derivatives, 1- and 3-substitutions of galactose. We have solved numerous protein-ligand crystal structures to study the effect of various substitutions. Fluorines are known to have diverse effects on physicochemical and conformational properties of ligands. Introduction of Fluorines at key positions in ligands has been proven to be promising strategy in lead optimization. Position and amount of fluorination has strong effect on the protein ligand interactions. Fluorines enhance ligand affinity by interacting with both the polar electropositive and hydrophobic groups in protein. Orthogonal multipolar C-F... C=O interactions with both peptide backbone and side chain carbonyls have been found important for Fluorines2. Distinct fluorophilic environments in proteins are the ubiquitous peptide bonds, which undergo multipolar C-F ... H-N, C-F ··· C=O, and C-F ··· H-CR interactions. Here we report several structures of galectin-3 CRD with mono-galactose based compounds having fluorines in different positions and numbers.

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Keywords: Galectin-3, Protein-ligand interactions, fluorines

MS06- Molecular machines and big complexes

Chairs: Prof. Guillermo Montoya, Prof. Kristina Djinovic Carugo

MS06-P01

Crystal structure of new [3]rotaxane

Damian Trzybiński¹, Mateusz Woźny², Sławomir Domagała¹, Krzysztof Woźniak¹

- 1, Biological and Chemical Research Centre, University of Warsaw, Warsaw, Poland
- 2. Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland

email: dtrzybinski@cnbc.uw.edu.pl

Discovery and development of mechanically interlocked molecular architectures (MIMAs) has opened up a completely new area of research. Such systems are used in construction of numerous artificial molecular devices (i.e. molecular switches, motors or shuttles). They could be applied in molecular electronics, materials chemistry, sensors, photonics or photoactive catalysis [1,2]. In the year 2016, Sauvage, Stoddart and Feringa were awarded the Nobel Prize in Chemistry for their pioneering work in this field, and there is still a great interest of chemists in design, synthesis and properties of new compounds belonging to this fascinating family of chemicals. Among the mechanically interlocked compounds, one of the most important place is occupied by the rotaxanes [3]. Compounds of this type are built from "dumbbell shaped molecule" threaded through a macrocycle or macrocycles. Here, we present the crystal structure of new [3]rotaxane (see schematic representation). It consists of two dibenzo-24crown-8 ether wheels and axle containing tetraazamacrocyclic complex coordinating the nickel ion. The identity of investigated compound was confirmed by the single-crystal X-ray diffraction analysis. Interestingly, in the case of (DB24C8)2/TAM system, the TAM unit is a π -acceptor and a hydrogen bond donor, which is reflected in the formation of specific molecular interactions between individual [3]rotaxane components, and influences its topology. The results of our study could be helpful to understand properties of the mechanically interlocked molecular compounds, especially polyrotaxanes.

Acknowledgements

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Keywords: [3]rotaxane, polyrotaxanes, mechanically interlocked molecular compounds

MS06-P02

Structural basis of ASPL-mediated regulation of p97 methylation by METTL21D

Sasa Petrovic1, Yvette Roske1, Udo Heinemann1

1. Macromolecular Structure and Interaction, Max Delbrück Center for Molecular Medicine, Berlin, Germany

email: spetrovic.mb@gmail.com

The ATPase p97/VCP (valosin containing protein) belongs to the family of AAA+ proteins (ATPases associated with diverse cellular activities). This essential and conserved protein family is involved in a broad range of cellular processes, such as DNA repair, cell cycle regulation, transcriptional activation, recombination, organelle biogenesis, ubiquitin-mediated protein degradation and homotypic membrane fusion (1). The function of p97 is regulated by a number of adaptor proteins and post-translational modifications (2). One example is the adaptor protein ASPL (alveolar soft-part locus), that has been investigated in further detail in our group, biochemically and structurally, showing that ASPL regulates p97 activity by reassembling it from a hexamer into a heterotetrameric complex containing two monomers of p97 and two molecules of ASPL (3).

The METTL21 family of methyltransferases is a novel class of methyltransferases dedicated to methylation of chaperones. METTL21D, also known as VCP-lysine methyltransferase (VCP-KMT), trimethylates p97 specifically at Lys315 (4). Overexpression of METTL21D has been shown to be present in number of human tumor tissues and able to increase the metastatic migration capability of several METTL21D knockout cancer cell lines (5). Trimethylated Lys315 is ubiquitously present in the intact hexameric form of endogenous p97 inside the pore, but it is inaccessible to METTL21D. ASPL promotes methylation (6) by disassembling the hexameric form of p97, thereby creating a new interaction interface for METTL21D.

Here we present the first crystal structure of a methyltransferase from the METLL21 family, METTL21D, bound to its target chaperone p97 in presence of its remodeling adaptor protein ASPL, adenosine-diphosphate (ADP) and the cofactor S-adenosyl-L-methionine (SAM). The structure reveals that METTL21D binds to the highly conserved second region of homology (SRH) motif of monomeric p97, in close proximity of the target site Lys315. The SRH motif serves as a recognition sequence for METTL21D, but the interaction extends to a larger surface of the D1 domain of p97. The structure shows the importance of p97 remodeling by ASPL and potentially other remodeling adaptor proteins to enable modification of inaccessible residues and to create new interaction interfaces.

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Keywords: p97 regulation, reassembly, methylation

MS06-P03

Structure-functional studies of protein P4 from bacteriophage φ8

Barbora Kaščáková¹, Zdenek Franta², Tatyana Prudniková², Michal Kutý², Roman Turna³, Ivana Kutá Smatanová²

- University of South Bohemia in České Budejovice, Institute of Chemistry and Biochemistry, České Budějovice, Czech Republic
- University of South Bohemia, Faculty of Science, Branisovska 1760, CZ-37005 Ceske Budejovice, Czech Republic, České Budějovice, Czech Republic
- University of Leeds, School of Chemistry, The Astbury Centre for Structural Molecular Biology, Leeds LS2 9JT, UK, Leeds, United Kingdom

email: baja227@azet.sk

The dsRNA bacteriophages of Cystoviridae family infect gram-negative Pseudomonas species bacteria [1]. The bacteriophages package their genome into empty capsid - procapsid, which protects the genome from degradation inside as well as outside host cell. The genome packaging is performed by a molecular motor - P4 proteins, which are components of procapsid [1, 2]. The P4s possess an NTPase activity that converts the chemical energy from ATP hydrolysis to a mechanical movement of packaging ssRNA precursors into a procapsid, where the replication and transcription of dsR-NA occurs [1, 3]. The P4s are RNA helicases belonging to the Superfamily 4 of helicases with characteristic presence of conserved sequence motifs (H1, H1a, H2, H3 and H4) [2, 3]. The RNA helicases cause the distribution of RNA-protein complexes and carry out RNA unwinding [2]. The P4 assembles into hexameric ring (Fig.1), which has on the outer perimeter NTP-binding sites and the nucleic acid binding sites are located in the central channel. Each P4 monomer consist of N-terminal, core NTPase domain with sequence motif and C-terminal domain. The C-terminal domain is inserted into the central channel of hexamer and its conformational changes regulate ring stability and ATPase activity of P4s [3]. Here we report our crystallization experiment results of the $\phi 8$ P4 protein crystals.



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Keywords: Bacteriophages, Protein P4,

MS07- Nucleic acids and interactions with proteins

Chairs: Prof. Ralf Ficner, Prof. Markus Wahl

MS07-P01

Purification and crystallization of novel archaean protein of the LSM family

Maryia Fando1, Natalia Lekontseva1, Alexey Nikulin2

- 1. Group of Structural Studies of Ribosomal proteins, Institute of Protein Research, Pushchino, Russia
- 2. Laboratory of Structural Studies of the Translation Apparatus, Institute of Protein Research, Pushchino, Russia

email: fando@vega.protres.ru

Lsm (Sm-like) proteins are found in representatives of all the three domains of life. They provide biogenesis and functioning of RNA molecules in the cells. Bacterial Lsm proteins called Hfq exhibit RNA-chaperone activity promoting interaction between regulatory sRNA and mRNA during regulation of translation [1], [2]. Eukaryotic Sm proteins are core proteins of the spliceosome while eukaryotic Lsm proteins are involved in the mRNA degradation [3]. Functions of the archaeal Lsm proteins (SmAP) in the cell have been studied pitiable, although there is some data on their participation in the processing of some. Our work concerns with structural and functional studies of an archaeal Lsm protein from Halobacterium salinarum. This protein has remarkable differences of the sequences compared with the homologues and, in fact, represents a minimal Lsm core. My current task is to determine the structure of the protein and its complexes with ribonucleotides and short RNA to define specificity and structural aspects of the Lsm-RNA interaction. We have obtained a genetic construct carrying the gene of the SmAP from H. salinarum (HsaSmAP). The protein was isolated and purified in preparative scale; it has been crystallized and a high-resolution diffraction dataset has been collected at ERSF in Grenoble. The work is supported by RFBR grant #18-04-00222.

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Keywords: Archaeal Lsm proteins, RNA binding, X-ray diffraction analysis

MS07-P02

Comparison of the uridine-binding site of hexameric and heptameric archaeal Lsm proteins

Natalia Lekontceva¹, Alisa Mikhailina¹, Svetlana Tishchenko¹, Alexey Nikulin¹

1. Institute of Protein Research RAS, Pushchino, Russia

email: lekontseva@vega.protres.ru

The Sm and Sm-like proteins are widely distributed among bacteria, archaea and eukarya. They are defined by the ability to adopt the Sm fold, which is comprised of a 5-stranded β-sheet and an N-terminal α-helix. They are participated in many processes connected with RNA-processing or regulation of gene expression. Hetero-heptameric eukaryotic Sm proteins form the core of the uracil-rich small nuclear RNPs that further assemble into spliceosomes and excise introns in eukaryotic pre-mRNAs. Homo-hexameric bacterial Lsm protein Hfq binds polyU RNA sequences in pockets between adjacent monomers at the central pore providing regulation translation of many mRNA. Archaeal Lsm proteins (SmAP, Sm Archaeal Protein) form homo-hexamers and homo-heptamers and appear to bind urudine-rich RNAs, nevertheless, the function of SmAP in the archaeal cells is not clear.

We compare structural organization of the uridine-binding site of SmAP from *Methanococcus jannaschii*, which forms hexamers, and SmAP from *Methanococcus vannielii*, which forms heptamers. The proteins were isolated and purified. Crystals of proteins and their complexes with ribonucleotides were obtained. Using the approach, which has been developed in our group, we analyze single-stranded RNA-binding sites on the surface of the proteins. Comparison of the obtained structures with the known SmAP structures in complex with RNA-fragments reveal significant differences in the RNA-binding site of the proteins.

This work was supported by Russian foundation for basic research (project #18-04-00222).

Keywords: Lsm protein family, archaea

The influence of nucleotide sequence of RNA 5' end on the electrostatic interaction energy of IFIT5 proteins with RNA

Urszula Budniak1, Paulina Dominiak1

1. Biological and Chemical Research Centre, Department of Chemistry, University of Warsaw, Warsaw, Poland)

email: ubudniak@chem.uw.edu.pl

The aim of my current project is to characterize electrostatic interactions in selected complexes of IFITs proteins with RNA with the use of the University at Buffalo Pseudoatom DataBank (UBDB). IFIT proteins (Interferon-induced proteins with tetratricopeptide repeats) are effectors of innate immune system, which are getting expressed in cell infected by viruses. By binding foreign RNA they prevent synthesis of viral proteins in human host cell. It has been shown, that IFIT1, IFIT2 and IFIT5 bind different forms of RNA (with triphosphate group or cap at 5' end of RNA), however literature data are not consistent about selectivity of IFITs protein and their preferred RNA forms. We want to verify the hypothesis of the lack of influence of RNA sequence on interaction energy in IFIT-RNA complexes.

Electrostatic energy usually has the most significant contribution to interaction energy (especially in the biological systems) and at the same time it can be calculated for large complexes, thus it is a perfect tool for estimating interaction energy in biomacromolecules. One of the more advanced methods to calculate electrostatic interaction energy is UBDB used together with Exact Potential Multipole Method (EPMM). UBDB enables reconstruction of charge density for macromolecules in quantitative manner. By UBDB+EPMM approach, which takes also charge penetration effects into account, it is possible to compute electrostatic energies with similar accuracy as with quantum chemistry methods, for wide range of types of interactions (hydrogen bonds, π - π stacking) and distances (not only at equilibrium geometry but also below or above). Calculations of energy are based on the structures of IFIT5 proteins deposited in Protein Data Bank (PDB) as 4HOR, 4HOS and 4HOT. After proper structure preparation, UBDB is transferred using LSDB program to reconstruct electron density distribution. Afterward, electrostatic interaction energy of protein-ligand complexes is calculated with EPMM method. Describing the nature of IFIT proteins interaction can help to expand our knowledge about mechanism of selective binding RNA and how human immune system recognizes and destroys viruses.

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Keywords: electrostatic interaction energy, UBDB databank, protein-RNA complexes

MS07-P04

HpDprA domains involved in interaction with DNA

Louisa Celma¹, Philippe Cuniasse¹, Dominique Durand¹, Johnny Lisboa¹, Dyana Sanchez¹, Stéphanie Marsin², Sophie Quevillon-Cheruel¹, Pablo Radicella²

- 1. Institute for Integrative Biology of the Cell (I2BC CEA, CNRS, Université Paris-Sud, F-91198 Gif-sur-Yvette, France
- Institute of Cellular and Molecular Radiobiology, IFJ, UMR967 CEA, INSERM, Universités Paris Diderot and Paris-Sud, F-92265 Fontenay-aux Roses, France

email: louisa.celma@i2bc.paris-saclay.fr

Natural transformation in bacteria is a horizontal gene transfer mechanism that allows exogenous DNA internalization and integration into the bacterial genome. The uptake of double-stranded DNA (dsDNA) from the outer environment is followed by the conversion of dsDNA to single-stranded DNA (ssDNA) and its transport into the cytoplasm (Mortier-Barrière et al., 2007). The transforming ssDNA is proposed to be bound and protected from the cytoplasmic nucleases by DprA (for DNA processing protein A) (Dwivedi et al., 2013). DprA is a ubiquitous protein in bacteria that has a key role in natural transformation process (Ando et al., 1999). In most bacteria, DprA is divided into three domains: a N-terminal domain, a conserved central domain and a C-terminal domain. In Helicobacter pylori, DprA (HpDprA) possesses only the central and the C-terminal domains (Ando et al., 1999). Functional analysis of HpDprA highlights the essential role of C-terminal domain in H. pylori natural transformation process.

In order to find the function of C-terminal domain in natural transformation process, an analysis of HpDprA's 3D structure was performed. This structure result of the data compilation arising from the X-ray structure of the central domain dimer, the NMR structure of the C-terminal domain, and the structure of the full-length DprA dimer obtained in solution by SAXS. Putative interaction sites between HpDprA and DNA were identified. Using a site directed mutagenesis approach, several mutants of HpDprA were generated. Electrophoretic Mobility Shift Assay shows that the isolated C-terminal domain is not able to interact neither with ssD-NA nor dsDNA, although its structural homology to winged helix DNA binding motifs. In contrast, the key residues of the central domain are crucial for both interactions. The cellular function of the C-terminal of HpDprA stays to be elucidated

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Keywords: HpDprA, DNA, Transformation

Insights into the chromosome partitioning system, ParABS

Yuh-ju sun¹

1. Institute of Bioinformatics and Structural Biology, National Tsing Hua University, Taiwan, Hsinchu, Taiwan

email: yjsun@life.nthu.edu.tw

Chromosome segregation is regulated by the ParABS system that is an important biological process in all domains of life. ParABS system includes ParA (an ATPase), ParB (a parS binding protein) and parS (a centromere-like dsDNA). The homologous proteins of ParA and ParB in Helicobacter pylori are HpSoj and HpSpo0J, respectively. We characterized the binding of parS and HpSpo0J and solved the crystal structure of the HpSpo0J-parS complex, with two HpSpo0J molecules bind with one parS. HpSpo0J interacts vertically and horizontally with its neighbors through the N-terminal domain to form an oligomer. These adjacent and transverse interactions might be needed for molecular assembly of a high order nucleoprotein complex and for ParB spreading. In addition, the ATPase activity of HpSoj was determined and the non-specific DNA binding of HpSoj dimer was detected. Based on these findings, we propose a structural model for the HpSoj and HpSpo0J complex in the ParABS partitioning system.

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Keywords: chromosome partitioning system, ParABS, segregation

MS07-P06

Nanocrystallization of the Nucleoid of Bacteria under Stress

Yurii Krupyanskii¹, Natalia Loyko¹, Ksenia Tereshkina¹, Vladislav Kovalenko¹, Eduard Tereshkin¹, Olga Sokolova², Alexander Popov³

- 1. Structure of Matter + Semenov Institute of Chemical Physics RAS, Moscow, Russia
- 2. Biological Faculty + Moscow State University, Moscow, Russia
- 3. ID-23-1 + European Synchrotyron Radiation Facility, Grenoble, France

email: vuriifkru@gmail.com

Structural, biochemical, and genetic changes caused by stress factors are known to be largely similar for cells of all modern organisms, which inherited the basic strategies of adaptation to different types of stress from their ancient ancestors. One of the strategies implemented in bacterial cells for constantly changing environmental conditions is related to the protection of the nucleoid from unfavourable environmental conditions by binding of DNA to specific histone-like proteins-DPS (DNA-binding protein from starved cells), in nanocrystalline complex, which helps to protect the nucleoid from damage and resume the activity of the bacterial cells later. The structure of these crystals within a cell was studied by use of synchrotron radiation on macromolecular crystallography station ID-23-1 as well as by use of transmission electron microscopy and tomography. However, the DNA conformation within these complexes has remained unsolved [1]. It was decided to decipher the structure of DNA-DPS crystals obtained in vitro which is in some respect the model of the structure of a nanocrystalline nucleoid. To this end crystalline complexes of DNA-DPS were studied with two different DNAs (one was linear and short DNA -24 b / p, the second was pBluescript SK (2958 b/p).) The crystal sizes reached 0.05 mm. The structure of the crystals of the DNA-Dps complexes (the resolution of this structure reaches 2.6 Å) is different from that previously published in the RCSB Protein Data Bank database. The crystal structure of the DNA-DPS complexes was slightly different for the different DNA length. At first superficial glance, one can speak of the absence of DNA molecules in a given crystal. Positions of DNA in our crystals, probably, were chaotic; this point explains why we miss the DNA on the obtained electron density map. Obtained results will allow us to get closer in understanding of the protection mechanism of biocrystallization inside a living cell.

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Keywords: biocrystallization, nucleoid, bacteria

Understanding native state of Cpf1 protein from *Francisella novicida* by small-angle X-ray scattering

Kyungjin Min1, Yuri Choi2, Hyung Ho Lee2

- 1. Seoul National University, Seoul, Korea South
- 2. Department of Chemistry, Seoul National University, Seoul, Korea South

email: km32479@snu.ac.kr

Clustered regularly interspaced short palindromic repeats (CRISPRs) from Prevotella and Francisella 1 (Cpf1) are RNA-guided endonucleases that produce cohesive double-stranded breaks in DNA by specifically recognizing thymidine-rich protospacer-adjacent motif (PAM) sequences. Even though, Cpf1 is emerging as a powerful genome-editing tool and numerous structures of various Cpf1 proteins have been solved, the apo-structure of Cpf1 remains elusive. In this study, to understand native state of Cpf1 protein from Francisella novicida (FnCpf1), we determined two solution structure of FnCpf1 with and without CRISPR RNA (crRNA) using small-angle X-ray scattering. Also, we visualized apo-structure of FnCpf1 using negative staining electron microcopy. By comparing between the apo-structure of FnCpf1 and with crRNA-bound structure, we realized that their overall shapes were similar as a closed form, suggesting that conformational change upon crRNA binding to FnCpf1 is not drastic, but a local induced fit might occur to recognize PAM sequences. However, the apo Cpf1 from Moraxella bovoculi 237 (MbCpf1) was examined as an open form, indicating that MbCpf1 may have a large conformational change for crRNA binding changing from an open to a closed form. These results suggested that the crRNA-induced conformational changes in Cpf1 differ among species.

Keywords: Cpf1, SAXS, electron microscopy

MS07-P08

Structural characterisation of diruthenium paddlewheel compounds with cytosinato and adeninato ligands

Josefina Perles¹, Ángela Valentín-Pérez², Santiago Herrero², Reyes Jiménez-Aparicio²

- Departamento de Química Inorgánica, Universidad Autónoma de Madrid, Madrid, Spain
- 2. Departamento de Química Inorgánica, Universidad Complutense de Madrid, Madrid, Spain

email: josefina.perles@uam.es

The interactions of dimetallic coordination compounds with biological molecules, in particular dirhodium and diruthenium metal-metal bonded complexes with paddlewheel geometry, are currently being invesigated as there is evidence indicating that dirhodium compounds covalently link with DNA, tRNA and proteins. In fact, paddlewheel diruthenium compounds can form metal-protein adducts, acting as inhibitors of C6 rat glioma cell proliferation or as inhibitors of glioma tumour growth *in vivo*. Open-padlewheel compounds have also been proved helpful for fingerprinting the junctions of RNA structure [1].

Recent works exploring the interactions of diruthenium moieties with biological species have focused on the elucidation of the coordination mode of the ruthenium atoms to the active sites of the potential ligands, as open-paddlewheel species have the tendency to include another bidentate ligand as a fourth bridge yielding a paddlewheel structure and thus gaining stability,

In this work, compounds $[Ru_2Cl(DPhF)_3(cyto)]$ and $[Ru_2Cl(DPhF)_3(ade)]$ have been synthesized and characterized by several techniques, including single crystal X-ray diffraction. Supramolecular interactions between these molecules have also been studied, paying particular attention to the intermolecular hydrogen bonds similar to the ones found in nucleic acids. Interestingly, it was found that compound $[Ru_2Cl(DPhF)_3(cyto)]$ is the first crystallographycally characterised ruthenium cytosinate, and the coordination mode found in $[Ru_2Cl(DPhF)_3(ade)]$ had not been previously described for adeninate (or adenine) in the crystal structure of a ruthenium complex.



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Keywords: Diruthenium paddlewheel compounds, antitumoral activity, supramolecular interactions

Structural insights into the dimeric human PNPase revealing why the disease-linked mutants exhibit lower RNA import and degradation activities

Bagher Golzarroshan¹, Hanna Yuan¹

1. Institute of molecular biology, Taipei, Taiwan

email: golzar1984@gate.sinica.edu.tw

Polynucleotide phosphorylase (PNPase) is an evolutionary conserved 3'-to-5' exoribonuclease that functions differently among species, ranging from RNA turnover in bacteria to RNA transport in mammals. In human, PNPase is essential for importing a subgroup of noncoding RNAs, including 5S rRNA, MRP RNA and RNase P RNA, into the mitochondria. Mutations in PNPase are thus linked to impair in the RNA import pathway and severe mitochondrial dysfunction and diseases. PNPase is primarily assembled into a trimeric conformation with a central channel for binding of a single-stranded RNA and leading its 3' end into the active site for degradation. In this study we show that the trimeric assembly of PNPase is affected by the disease-linked mutations, including Q378R and D475G. PNPase is oligomerized into a dimeric conformation after introducing the disease-linked mutations, and these PNPase mutants have lower RNA-binding and degrading activities as compared to the wild-type PNPase. Moreover, we found that S1 domain of PNPase is responsible for the interaction with the stem-loop motif of imported RNAs. We further determined the crystal structure of the dimeric form of the S1-truncated PNPase at a resolution of 2.8 Å. Combining with small angle X-ray scattering (SAXS), we showed that both of the RNA-binding KH and S1 domains are not fully accessible in the dimeric structure, explaining why these dimeric PNPase mutants interact with RNA poorly. Taken together these results show that mutations at the interface of the trimeric PNPase tend to produce a dimeric protein with obstructed RNA-binding surfaces, thus impairing both of its RNA import and degradation activities and leading to mitochondria disorders.

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Keywords: Crystal Structure, Diseases, Nucleic Acid

MS08- Membranes and membrane interacting proteins

Chairs: Prof. Susanna Törnroth-Horsefield. Prof. Adrian Goldman

MS08-P01

Structure of an essential inner membrane protein-LPS complex

Thomas Clairfeuille¹, Kerry Buchholz², Jian Payandeh¹, Steven Rutherford²

- 1. Department of Structural Biology, Genentech, South San Francisco, United States of America
- 2. Department of Infectious diseases, Genentech, South San Francisco, United States of America

email: clairfet@gene.com

Multi-drug resistant Gram-negative bacteria (GNB) represent a global health threat and urgent unmet medical need. A defining feature of GNB is their outer membrane (OM). where lipopolysaccharide (LPS) establishes a permeability barrier that notoriously frustrates most antibiotic discovery efforts. LPS is also a potent stimulator of the innate immune system and responsible for a growing number of deaths, where ~5 million childhood deaths are attributed to bacterial sepsis every year. Despite the clear biomedical and pharmacological relevance of LPS, the essential mechanisms that coordinate LPS and phospholipid transport to the OM remain unknown. During efforts to identify new targets for the treatment of GNB, we became focused on a multipass integral inner membrane protein of unknown function that we call PlbA. Here, we find that PlbA is essential to establish infection in Escherichia coli, and that PlbA depletion produces defects in the OM barrier. High-resolution X-ray crystallographic structural analyses using traditional and XFEL diffraction methods of PlbA identifies a superfamily of transmembrane proteins that catalyze diverse modifications in the envelopes of Gram-positive and Gram-negative bacteria. However, the unique architecture of PlbA reveals a defunct active site. Instead, an LPS molecule is selectively coordinated to an unanticipated LPS-binding motif found along the periplasmic membrane leaflet of PlbA, where core-lipid A binding is achieved through an intricate network of backbone and water mediated interactions. Notably, this PlbA-LPS interaction complex is unprecedented when compared to known structures of selective LPS binding proteins, including the LPS transporter MsbA and the immune Toll-like receptor TLR4. Introduction of disruptive single point mutations at the PlbA-LPS interface leads to defects in the OM barrier. Overall, this work reveals unprecedented insight into the structural basis of LPS perception within the inner membrane of GNB and implicates PlbA as an LPS-sensor that helps coordinate LPS and PL transport to the OM.

Keywords: lipopolysaccharide, outer membrane, lipid transport

MS08-P02

Structural insight into protein-aided bacterial biofilm formation

Yvette Roske¹, Anne Diehl², Linda Ball², Kürsad Turgay³, Udo Heinemann¹, Ümit Akbey⁴, Hartmut Oschkinat²

- 1. Max-Delbrück-Center for Molecular Medicine, Berlin, Germany
- 2. Leibniz-Forschungsinstitut für Molekulare Pharmakologie, Berlin, Germany
- Institut f
 ür Mikrobiologie, Leibniz Universit
 ät Hannover, Hannover, Germany
- 4. Aarhus Institute of Advanced Studies, Aarhus University, Aarhus, Denmark

email: yroske@mdc-berlin.de

Microorganisms form surface-attached communities, termed biofilms, which can serve as protection against host immune reactions or antibiotics. *Bacillus subtilis* biofilms contain TasA as major proteinaceous component in addition to exopolysaccharides. In stark contrast to the initially unfolded biofilm proteins of other bacteria, TasA is a soluble, stably folded monomer, whose structure we have determined by X-ray crystallography.

In this work, we present a high-resolution crystal structure of soluble, monomeric TasA in its mature secreted form. Despite its apparent homology to camelysins, biochemical experiments suggest that TasA is not an active protease. As a basis for understanding the structural changes occurring during fiber and biofilm formation, the monomer and multimeric forms were investigated in vitro and in vivo by NMR, analytical ultracentrifugation (AUC), and other biophysical techniques. In particular, we analyzed in vitro the transformation of soluble monomeric TasA into two different states, a gel-like form and fibrils. Magic-angle spinning (MAS) NMR applied to biofilms that were generated by adding soluble, monomeric and isotope-labeled TasA to the medium of B. subtilis AtasA cultures allowed probing of the in vivo situation, revealing the formation of homogeneous TasA fibers as the major proteinaceous extracellular matrix component. Thereby, we characterized the transition of folded TasA into fibrils, both in vitro and in its natural biofilm environment on a molecular level.

Understanding the formation and structure of protective bacterial biofilms will help to design and identify antimicrobial strategies. Our experiments with the secreted major biofilm protein TasA characterize on a molecular level in vivo the transition of a folded protein into protease-resistant biofilm-stabilizing fibrils. Such conformational changes from a globular state into fibrillar structures are so far not seen for other biofilm-forming proteins. In this context, TasA can serve as a model system to study functional fibril formation from a globular state.

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Keywords: TasA, structure, biofilm

MS08-P03

X-ray solution scattering and crystallization experiments towards time-resolved structural studies of the membrane protein transporter, Mhp1

Diogo Melo¹, Maria Kokkinidou¹, Yun-yun Gao¹, David Sharples², Peter J.F. Henderson², Arwen R. Pearson¹

- Hamburg Centre for Ultrafast Imaging & Institute for Nanostructure and Solid-state Physics, University of Hamburg, CFEL, Hamburg, Germany
- 2. Astbury Centre for Structural Molecular Biology, University of Leeds, Leeds, United Kingdom

email: diogo.melo@desy.de

Secondary-active trans-membrane transporters facilitate the movement of essential substrates, such as neurotransmitters or metabolites, across the cell membrane. Disruption of these vital processes is implicated in severe diseases in humans, e.g. Parkinson's disease. Our aim is to investigate the structural basis of the transport mechanism of secondary-active transporters, using the bacterial sodium-hydantoin transporter Mhp1 [1] as a model system examined by serial time-resolved crystallographic methods. Mhp1 has been previously crystallized in two crystal forms in its outward $(P2_12_12_1)$ and inward $(P6_1)$ facing conformations, and soaking experiments have so far only shown substrate bound in the outward facing cavity, suggesting that crystal packing may limit the ability of the transporter to complete its full structural cycle in the crystalline state. Interestingly, SEC-SAXS experiments suggest that different buffer conditions result in the formation of differently arranged small oligomers (< 6 monomers) that may result in distinct crystal forms. We are therefore exploring the use of SEC-SAXS as a tool to guide the choice of crystallization conditions in order to obtain crystal packing arrangements that will enable the structural transitions associated with substrate transport. References:

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Keywords: Membrane protein transporters, SEC-SAX, oligomers.

MS09- Enzymology

Chairs: Prof. Leila Lo Leggio, Dr. Dusan Turk

MS09-P01

Insights into the structural background and mechanism of inhibition of dUTPases by a proteinaceous inhibitor

Andras Benedek¹, Fanni Temesvary-Kis², Tamjidmaa Khatanbaatar², Ibolya Leveles², Beata Grolmusz Vertessy¹

- Department of Applied Biotechnology, Budapest University of Technology and Economics and Institute of Enzymology, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Budapest, Hungary
- 2. Department of Applied Biotechnology, Budapest University of Technology and Economics, Budapest, Hungary

email: benedek.andras@ttk.mta.hu

The dUTPase enzyme family plays a key role in maintaining genomic integrity throughout preventing uracil incorporation into DNA (1). Their importance is underlined by their presence in almost all type of organisms from bacteria to primates. Their dysfunction poses severe consequences to most cells or organisms, since increased uracil incorporation leads to DNA double strand breaks and eventually cell death via hypersensitization of the uracil base excision repair process. Therefore dUTPases are regarded as chemotherapeutic targets in certain diseases like tuberculosis and malaria, and also in some aspects of cancer treatment (2,3). To design effective, species-specific dUTPase inhibitors with minimal side-effects, it is essential to explore carefully any structural differences among dUTPase homologues encoded by different species.

A recently discovered staphylococcal protein termed Stl is able to inhibit a couple of dUTPase homologues (4,5). However, its inhibitory potential may be different according to species-specific structural differences among dUTPases. We have pointed out that protein Stl which was originally identified as a bacterial repressor is also able to form a stable protein complex with the eukaryotic *Drosophila melanogaster* dUTPase and inhibit remarkably its enzymatic activity (6).

Our results indicated that the amino acid side-chains being involved in this interaction are partially evolutionarily conserved among bacterial and eukaryotic dUTPase homologues. Interestingly, we have also found that while Stl forms a strong complex with *Escherichia coli* dUTPase, still, no inhibition of this dUTPase was observed – this is exceptional among the numerous investigated complexes (4,5,6,7). Consequently we became committed to uncover the structural bases for the lack of enzymatic inhibition upon complex formation in the *E. coli* dUTPase.

Relying on our recent results regarding the interaction surface of the human dUTPase and protein Stl (7), we designed a rational mutation screen. We identified specific amino acid side-chains in the *E. coli* dUTPase sequence as potentially relevant factors for the lack of inhibition, and found that among the generated mutants, two became sensitized to Stl-induced inhibition. We successfully grew crystals from these mutants and obtained a complete X-ray diffraction dataset at 2.5 Å resolution for one of these. The structure is being solved and will be presented at the conference - it is expected to provide key novel insights into the mechanism of StI induced dUTPase inhibition.

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Keywords: dUTPase, inhibitor, mutagenesis

On the versatility of CLECs for biotechnological applications, from micro to macro-fluidics devices

José A. Gavira¹, Cristobal Verdugo-Escamilla¹, Sergio Martínez-Rodríguez ², Isaac Rodríguez-Ruiz³, Mayte Conejero-Muriel¹

- 1. LEC, IACT, CSIC-UGR, Armilla, Granada, Spain
- Dpto. Bioquímica y Biología Molecular e Inmunología (UGR), Melilla, Spain
- 3. CEA, DEN, DMRC, SA2I, Bagnols-sur-Cèze, France

email: jgavira@iact.ugr-csic.es

Biocatalysts make use of the versatility, selectivity and specificity of enzymes to catalyze a variety of processes for the production of relevant compounds under mild conditions. One of the most common strategies to extend the lifetime under extreme conditions and to increase the efficiency of enzymes is their immobilization in different materials or the auto-immobilization by cross-linking. In this context, Cross-Linked Enzyme Crystals (CLECs), yet proven to be a better solution to enhance catalyst lifetime or recoverability when compared with Cross-Linked Enzyme Aggregates (CLEAs), were almost abandoned [1]. However, a look into the literature reveals a renaissance in the interest on this methodology, probably boosted by the extensive knowledge gained during the last two decades in protein crystallization, highly decreasing its cost and laboriousness [2]. We have recently demonstrated that the use of CLECs-based microreactors shows unprecedented self-storage capability and stability as compared to standard biosensors, which cannot be stored for long periods due to quick denaturation of the enzymes (with lifetimes of weeks in the best case) [3]. We have further extended this concept by combining an enzymatic lipase microreactor, operating in continuous mode, with an optofluidic detection system [3] (Fig. a). The use of enzymatic catalytic reactions under microfluidic flow conditions reveals a promising technology with a number of strategic advantages: improvement of surface/volume ratios, enhanced energy consumption and mass transport, fundamental for the fabrication of CLECs-based biosensor systems. Furthermore, we have produced a packed 10 cm-chromatographic column with Reinforced Cross-Linked Lipase Crystals (RCLLCs), demonstrating a scale-up representation of the microfluidic approach that also operates in continuous flow (Fig. b-c). In this work, we will summarize our most recent results in the biotechnological application of enzyme crystals using both the micro and macro scale flow systems.

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Keywords: CLECs, Reinforced-cross-linked-enzyme-crystals, lipase

A bioconjugate of lipase with polypyrrolemethyl anthranilate functionalized "wormlike" titanium dioxide nanocomposite as promising nanobiocatalyst

Mohd Shamoon Asmat1, Qayyum Husain1

1. Department of Biochemistry, Aligarh Muslim University, Aligarh, Aligarh, India

email: shamoonasmat@gmail.com

Recently the development of unique nanoscaffolds have gained quite an attention for the preparation of highly stable nanobiocatalysts in order to exploit them for the synthesis of novel compounds and biodiesel. Biodiesel is a key paradigm towards the development of sustainable environment in the future. We show this by the fabrication of novel polypyrrole-methyl anthranilate functionalized titanium dioxide nanomaterial and its conjugation to lipase for the synthesis of flavoured compound and potential in biodiesel synthesis. We demonstrated successful immobilization of lipase from Rhizopus oryzae on a Ppy-MA/TiO2 NM by physical adsorption and a glutaraldehyde-activated covalent coupling procedure. The catalytic efficiencies of the free and immobilized preparations were determined for the hydrolysis of p-nitrophenyl palmitate. The covalently immobilized lipase displayed a significantly higher activity yield (effectiveness factor of 0.97) in comparison with the adsorbed counterpart (effectiveness factor of 0.86). The binding of lipase to the Ppy-MA/TiO2 NM was confirmed by transmission electron microscopy, Fourier transform infrared spectroscopy and scanning electron microscopy. TGA and DTA were performed to investigate the thermal stability of the synthesised biocatalysts. The storage stability, solvent tolerance, and reusability of the resulting nanobiocatalyst and the effect of pH and temperature on its catalytic activities were also investigated. The prepared nanobiocatalysts displayed remarkably improved activity in terms of solvent tolerance (activity recovery of 150% and 125% in acetone and isopropanol, respectively) in comparison with its free counterpart. We envisage that the covalent binding method played a profound role in enhancing the properties of the enzyme immobilized on the Ppy-MA/TiO2 NM. The immobilized lipase successfully synthesised flavour ester in solvent free media and n-hexane having 25.5% and 85.5% ester yields respectively and also holds vital potential for enzymatic biodiesel synthesis. Molecular docking results confirmed the successful conjugation of the enzyme-nanocomposite complex.

Keywords: Nanobiocatalyst, Molecular docking, Flavor synthesis

MS09-P04

Crystal structure of inositol 1,3,4,5,6-pentakisphosphate 2-kinase from *Cryptococcus neoformans*

Sangkee Rhee¹, Juntaek Oh¹, Dong-Gi Lee², Yong-Sun Bahn²

- 1. Department of Agricultural Biotechnology, Seoul National University, SEOUL, Korea South
- 2. Department of Biotechnology, Yonsei University, SEOUL, Korea South

email: srheesnu@snu.ac.kr

The fungal pathogen Cryptococcus neoformans is a causative agent of meningoencephalitis in humans. For its pathogenicity, the inositol polyphosphate biosynthetic pathway plays critical roles. In particular, an inositol 1,3,4,5,6-pentakisphosphate 2-kinase (Ipk1) catalyzes the phosphorylation of IP5 to form IP6, a substrate for subsequent reaction to produce inositol pyrophosphates, such as PP-IP₅/IP₇. In fact, deletion of IPK1 significantly reduces the virulence of C. neoformans, indicating that Ipk1 from C. neoformans (CnIpk1) is a major virulence contributor. We initiated structural analysis of CnIpk1 to provide structural information for the possible development of drug design for treatment of cryptococcosis. A crystal structure of the unliganded CnIpk1, the first structure for a fungal Ipk1, will be presented at 2.35 Å resolution. Structure comparisons of CnIpk1 with those from Arabidopsis thaliana and Mus musculus suggest structural similarities and discrepancies for fungal Ipk1 among members of the Ipk1 family. This work was supported by Next Generation BioGreen 21 program of Rural Development Administration (Plant Molecular Breeding Center) of Republic of KOREA.

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Oh, J. Lee, D.-G. Bahn, Y.-S. & Rhee, S. (2017) J. Struct. Biol. 200, 118-123.

Keywords: inositol 1,3,4,5,6-pentakisphosphate 2-kinase; Cryptococcus neoformans; crystal structure

Crystal structures of *Serratia marcescens* reveal a homotetramer and insight into a flexible catalytic cleft

Wen-Ching Wang¹

1. Department of Life Science, National Tsing Hua University, Hsinchu, Taiwan)

email: wcwang@mx.nthu.edu.tw

The short-chain dehydrogenase/reductase (SDR) from erratia marcescens BCRC 10948 (SmSDR) that catalyzes an asymmetric reduction of alkyl ketones to the corresponding chiral alcohols is capable of converting 1-(3-hydroxyphenyl)-2-(methylamino) ethanone (HPMAE) into (R)-phenylephrine, which is marketed medically as a nasal decongestant agent. Here, we report the crystal structure of the apo-form SmSDR solved to 1.47 Å. The SmSDR structure shows a homotetramer of which each subunit consists a nucleotide-binding Rossmann domain and a presumed binding pocket surrounded by five loops and an helix (α 7). Phe98 and Phe202 stand on the α 7 helix and loop b4-a4) and form hydrophobic contacts with nearby residues. Site-directed mutagenesis characterization (WT, F98Y, F98YF202Y, and F98YF202L) revealed that F98YF202L exhibited a higher transformation activity toward HPMAE. Crystal structures of F98AF202L SmSDR, F98LF202L NADPH, and F98Y-F202Y variants show an overall homologous structure. Substitution of F98 with alanine leads to the loss of the hydrophobic contacts between two arms, whereas F98YF202Y creates a strong H bond. In addition, the whole-cell conversion of F202A had an increased yield (1.9-fold) than that of WT. Together, our results suggest a robust structure-guided approach to stabilize the binding pocket that can be used to generate a valuable SmSDR variant for pharmaceutical applications.

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Keywords: short-chain dehydrogenase/reductase), Serratia marcescens BCRC 10948, (R)-phenylephrine

MS09-P06

Crystal structure of PigA, a prolineoxidizing enzyme in prodigiosin biosynthesis

Cheng-Chung Lee¹, Tzu-Ping Ko¹, Chwan-Deng Hsiao², Andrew H.-J. Wang¹

Institute of Biological Chemistry, Academia Sinica, Taipei, Taiwan
 Institute of Molecular Biology, Academia Sinica, Taipei, Taiwan

email: chengung@gate.sinica.edu.tw

Prodigiosin is an intensely red pigment comprised of three pyrroles. The biosynthetic pathway includes a two-step proline oxidation catalyzed by PigA, using FAD as its cofactor. Here the enzyme is crystallized in apo and FAD-bound forms. The protein folds into two α-helical domains (I and III) separated by a β -sheet domain (II) and it belongs to the acyl-CoA dehydrogenase (ACAD) family. In the tetrameric enzyme, which comprises two dimers associated via domain III, FAD is located in a cleft surrounded by all three domains of one monomer and domain III of another. The overall structure as well as the FAD-binding mode is similar to those of other ACAD-family enzymes. Alternate backbone conformations in the N-terminal part of helix aG correlate well with the expected location of substrate to the Re side of FAD. Complex modeling with PigG, the acyl carrier protein, suggests a plausible binding mode. The structure helps explain the proline oxidation mechanism, in which Glu244 plays a central role in the double-bond formations. It also reveals a plausible pocket for oxygen binding and reduction on the Si side of FAD.

Keywords: Prodigiosin, proline-oxidizing, PigA

Crystal structures of Bowman-Birk Inhibitor in complex with α-chymotrypsin

Eva Johansson¹, Christian Wenzel Tornøe¹

 Department of Protein and Peptide Chemistry 1, Novo Nordisk A/S, Måløv, Denmark

email: evjh@novonordisk.com

Bowman-Birk Inhibitor (BBI) protein from soy bean is a serine protease inhibitor of 71 amino acid residues containing seven disulphide bonds. It has two distinct 9 amino acid loops which inhibit α -chymotrypsin and trypsin, respectively. Chemical protein synthesis, using a divergent strategy, was used to prepare analogues of BBI to improve α -chymotrypsin inhibition. Four BBI analogues were prepared, and a four-fold improvement in chymotrypsin inhibition was obtained. Crystal structures of co-crystallised α -chymotrypsin:BBI complexes were determined for both wtBBI from soy bean and synthetic 27L,42T,43F,45I,47P-BBI variant. The crystal structures confirmed the correct protein fold of the synthetic BBI and showed a similar overall structure to the wtBBI.

The improved inhibition of α -chymotrypsin by the modified BBI may be explained comparing the two complex structures. The entire Phe43 amino acid residue is clearly pulled further into the chymotrypsin P1 pocket. This also results in withdrawal of the Thr42 backbone carbonyl group preventing a hydrogen bond formation across the inhibitory loop present in the α -chymotrypsin:wtBBI structure. However, the A42T modification provides the possibility of an alternative hydrogen bond formation utilising the threonine residue side chain hydroxyl group instead of the backbone carbonyl. Furthermore, the introduction of the Pro47 residue makes the structure more rigid and facilitates the hydrogen bond formation the formation mentioned above.

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Tornøe, C., Johansson, E. & Wahlund, P.-O. (2017) Synlett, 28, 1901-1906

Keywords: Bowman-Birk inhibitor, chymotrypsin, chemical protein synthesis

MS09-P08

pH dependent conformational changes of β-amylase/glucose complex crystal measured at room temperature

Bunzo Mikami¹, Xueni Hou¹, Kotaro Mori¹, Adachi Motoyasu², Kimihiko Mizutani¹, Nobuyuki Takahashi¹

- 1. Graduate School of Agriculture, Kyoto University, Uji, Kyoto, Japan
- 2. Japan Atomic Agency, Tokai-mura, Ibaraki, Japan

email: mikami@kais.kyoto-u.ac.jp

β-Amylase catalyzes the liberation of maltose from the non-reducing ends of starch. In contrast to a-amylase, b-amylase produces β-anomeric maltose, and is classified as an inverting enzyme. In soybean β-amylae (SBA), the hydrolysis of the α -1, 4-glycosyl linkage is proceeded by two catalytic residues, Glu186 (acid) and Glu380 (base) where the substrate binding site consists of five subsites (-2, -1, +1, +2 and +3). Near this active site, the enzyme has two mobile loops, flexible loop (residue 96-103) and inner loop (residue 341-345). The conformation of these loops change from open to closed form and from apo to product form, respectively, during enzyme action. The side-chain of Lys295 also changes conformation from apo to complex form. In this paper, we are intended to determine the structural changes of SBA/G1 (glucose) complexes in a different pH media. We have determined the crystal structure at room temperature to avoid the undesirable effect of freezing and cryo-protectant. SBA was crystallized by a hanging-drop vapor diffusion against 1 ml of the bottom solution containing 45% saturated ammonium sulfate, at pH 5.4 and 4°C. The obtained crystals were packed in glass capillaries after soaked with 0~300mM G1 in the different pH media for 30min at 20°C. The diffraction data sets were collected at 20°C with a MX225HE (Rayonix) detector at BL26B1 beam-line in SPring-8. The crystal belonged to P3,21 with cell dimensions of a = b = 84-85 and c = 144-145 Å. The crystal data were collected with 98-100 % completeness and R_{merge} of 0.04-0.07 up to 1.6-1.9 Å resolution. The models were refined with SHELXL with R = 0.13-0.14 and $R_{free} =$ 0.15-0.17. At pH 3.95, two G1 molecules were located at the subsites -2 and +2 with open flexible loop, apo inner loop and apo form of Lys295, whereas at pH 7.9, three G1 molecules were found at subsites -2, +1 and +2 with closed flexible loop, product form of the inner loop and complex form of Lys295 (Fig. 1). These results indicate that the conformational change of the inner loop and the side-chain of Lys295 depend on the G1 binding at +1 site. We are now trying to determine the dissociable residue controlling the sugar binding and the conformational changes of the active site



Keywords: β -amylase, enzyme reaction, enzyme/substrate complex

Structure analysis of haloalkane dehalogenase DbeA ΔCl variant from *Bradyrhizobium elkanii* USDA94

Tatyana Prudnikova¹, Pavlina Rezacova^{1,2}, Radka Chaloupkova³, Jiri Damborsky³, Ivana Kuta Smatanova⁴

- 1. Institute of Organic Chemistry and Biochemistry, South Bohemia University, Ceske Budejovice, Czech Republic
- 2. Institute of Molecular Genetics, Academy of Sciences of the Czech Republic, Prague, Czech Republic
- Loschmidt Laboratories, Department of Experimental Biology and Research Centre for Toxic Compounds in the Environment, Faculty of Science, Masarvk University, Brno, Czech Republic
- 4. Faculty of Science, University of South Bohemia , Ceske Budejovice, Czech Republic

email: talianensis@gmail.com

A novel enzyme, DbeA, belonging to the family of haloalkane dehalogenases (EC 3.8.1.5) was isolated from Bradyrhizobium elkanii USDA94. This haloalkane dehalogenase is closely related to DbjA enzyme from Bradyrhizobium japonicum USDA110 (71% sequence identity), but has different biochemical properties. DbeA is generally less active and has a higher specificity towards brominated and iodinated compounds than DbjA. The DbeA protein was crystallised using the sitting-drop vapour-diffusion method and the crystal structure of a DbeA enzyme has been solved and deposited at Worldwide Protein Data Bank under PDB ID 4k2a. The DbeA wt structure revealed the presence of two halide-binding sites. The first chloride-binding site is located in the active site in between two halide-stabilizing residues. The second halide-binding site is unique to DbeA and has not been previously reported in any other structure of this enzyme family. To elucidate the role of the second halide-binding site, a two-point variant DbeA ΔCl (I44L+Q102H) lacking this site was constructed and biochemically characterized [1]. Elimination of the second halide-binding site decreased the stability and catalytic activity, and dramatically altered the substrate specificity. The two-point substitution resulted in a shift of the substrate-specificity class, which is the first time this has been demonstrated for this enzyme family. Rational design of buried halide-binding sites represents a novel strategy for engineering of enzymes with modified catalytic properties.

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Keywords: Haloalkane dehalogenase, second halide binding site and halogenated compounds
A novel direct link between Ca²⁺-signaling and energy homeostasis?. Structural background of brain and muscle creatine kinase modulation by calmodulin

Janina Sprenger¹, Jenny Bredtfelt², Ann-Victoria Isaak³, Neal Patel³, Ashley Vanderbeck³, Leila Lo Leggio⁴, Karin Åkerfeldt³, Sara Snogerup Linse²

- 1. University of Copenhagen, Copenhagen, Denmark
- 2. Department of Biochemistry and Structural Biology, Lund University, Lund, Sweden
- 3. Haverford College, Haverford, United States of America
- Department of Chemistry, University of Copenhagen, Copenhagen, Denmark

email: jasp@chem.ku.dk

Creatine kinases (CKs) are important players in the energy homeostasis especially of cells with a high ATP turnover such as in brain and muscle. The cytosolic brain CK (CKB) and muscle CK (CKM) are two isoforms which, depending on the substrate concentrations, convert reversibly ATP and creatine (Cr) into creatine-phosphate (CrP) and ADP, forming togather with the mitochondrial isoforms an efficient ATP shuttle- and buffering system.

We have previously reported possible interaction of calmodulin (CaM) with CKB and the other isoforms (Herling et al., 2016) and showed that CaM binds in presence of Ca²⁺ to CKB with an affinity (K_D) in the low micro-molar range. Kinetic measurements following ATP production by CKB in presence and absence of Ca²⁺-CaM revealed that the native positive cooperativity of the CK reaction is abolished by Ca²⁺-CaM binding, leading to an ~10 fold increase in ATP production at physiological CrP-concentrations. Another link between Ca²⁺ signaling and CKB has previously been reported where calmodulin-activated protein kinases N-terminally phosphorylate CKB that is then recruited to the ER-membrane but without changing its kinetics, suggesting a regulation by CaM through CKB through localization (Schlattner et al., 2016).

Recently we identified the CaM binding sites in CKB and CKM that are homologous, dynamic regions within the C-terminal domains in close proximity to the active sites. We succeeded in crystallizing the complexes of CaM with the peptides corresponding to the CaM binding sites of CKB and CKM. High resolution structures were obtained (1.2 Å and 1.4 Å, respectively), that show for both peptides a novel 1:2 (CaM:peptide) extended binding mode with CaM, though with different orientations of the peptides in the C-terminal domain (see figure). ITC studies confirm the binding modes in solution where each CaM-lobe independently can bind one peptide with affinities in the low micro-molar range. The new structural insights into the CaM-CKB/CKM interaction may help to explain how the the activities of CK in muscle and brain tissue can be regulated directly by CaM to provide increased amounts of ATP from CrP resources for high energy consuming processes during Ca2+ release. Furthermore the novel CaM binding mode opens new avenues for protein engineering and we are exploring possibilities to use this interaction as fusion proteins to locate and order small proteins within highly porous protein crystals as a system to determine structures based on X-ray diffraction.



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Keywords: Creatine kinase regulation, Calmodulin-peptide structure, Allostery

Structural aspects of specie specific moonlighting functions of dUTPases

Ibolya Leveles¹, Beáta G. Vértessy¹, Judit Tóth², Kinga Nyíri¹, Ábris Bendes³ Anna Lopata¹

- Budapest University of Technology and Economics, Department of Applied Biotechnology and Food Science, Budapest, Hungary
- Research Centre for Natural Sciences, Institute of Enzymology, Budapest, Hungary
- Univerity of Oulu, Faculty of Biochemistry and Molecular medicine, Oulu, Finland

email: leveles.ibolya@ttk.mta.hu

dUTPases constitute an enzyme family which has a sanitizing role by preventing the incorporation of noncanonical bases in the DNA. The catalytic mechanism of action of these enzymes has been revealed for a number of representatives in clear structural and kinetic detail.

However there are several specie specific moonlighting functions, which allow a fine tuned drug design on different malignant cases, dUTPases being a preferred drug target.

One of our well studied protein is the *Mycobacterium tuber-culosis* dUTPase.

The main catalytic function has been detailed by clear structural proof of a conserved aromatic stacking interaction between dUTPase and its nucleotide substrate which largely contributes to the stabilization of the associative type transition state of the nucleotide hydrolysis reaction.

Further, X-ray structures of mutant proteins revealed the importance of the five amino acids long extra loop, specific to mycobacteria, that is proven to be a target in anti-tuberculotical drug design.

In Staphylococcus, phage dUTPases are also suggested to be involved in a moonlighting function regulating the expression of pathogenicity-island genes. Staphylococcal phage trimeric dUTPase sequences include a specific insertion that is not found in other organisms. The phage-specific insert segment of Phi11 phage dUTPase folds into a beta-pleated mini-domain resembling a distorted Greek-key motif. This small structural motif is very common in protein-folding cores. Comparison of the presently available sequences of staphylococcal phages encoding trimeric dUTPases reveals

that the presence of such inserts seems to be general and that subgroups of phages can be distinguished based on the segment characteristics.

The binding partner staphylococcal repressor protein Stl_{SaPL}. $_{Bovl}$ (Stl) forms strong complex with both staphyllococcal and human dUTPase. Recent structural, functional analysis studies reveal that this interaction results in significant reduction of both dUTPase enzymatic activity and DNA binding capability of Stl.



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Keywords: dUTPase, sanitizing, moonlighting

Structural insights into an evolutionary intermediate of dUTPase

Beata Vertessy¹, Andras Benedek², Ibolya Leveles

- BME ABÉT Budapest University of Technology and Economics, Budapest, Hungary
- 2. BME ABÉT, Budapest, Hungary

email: vertessy@mail.bme.hu

The enzyme family of dUTPases are involved in preventive DNA repair by sanitizing the dNTP pool via hydrolyzing dUTP into dUMP and inorganic pyrophosphate (1). Metagenomic analyses revealed that dUTPases are present in samples isolated from extreme conditions with regard to pollutants, salt and thermal conditions (2). As to present, two major families of dUTPases are described. On the one hand, beta-sheeted subunits form a symmetric trimer wherein the three active sites are constituted by conserved sequence motifs from all the three subunits. On the other hand, alpha-helical subunits form a dimeris arrangement with active sites situated at the dimer interface.

We found that the within the trimeric dUTPase fold, several organisms encode the respective gene that contains three copies of the subunit in a linked arrangement such that the resulting protein product contains the three subunits in covalent linkage within one single polypeptide chain. The evolutionary pathway leading the the triplication of the ancient dUTPase gene necessarily involves a dimeric evolutionary intermediate (3).

Here we investigate if such evolutionary intermediate dUT-Pase enzyme may function as a catalytically active species, in constrast to the general arrangement of this enzyme family. We characterize the dimeric enzyme using enzyme kinetics and biophysical techniques. We also crystallize this evolutionary intermediate and provide structural insights into the organization of the active site.

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Keywords: folding, homology, dUTPases

MS09-P13

Bacterial metal-dependent DNase with novel fold

Jan Dohnalek¹, Jan Stránský¹, Vojtěch Andrle¹, Mária Trundová¹, Tomáš Koval¹, Lars Østergaard²

- Laboratory of Structure and function of biomolecules, Institute of Biotechnology of the Czech Academy of Sciences, Vestec, Czech Republic
- Department of Agile Protein Screening, Novozymes A/S, Bagsvaerd, Denmark

email: dohnalek007@gmail.com

Bacillus licheniformis produces extracellular DNase NucB capable of double-strand DNA cleavage [1]. NucB is a sporulation-specific enzyme with so far unknown specificity and structure-function properties. NucB was successfully produced using bacterial expression, purified, crystallized and diffraction data were collected using synchrotron radiation and a MetalJet in-house X-ray source [2]. Systematic optimization of the key S-SAD protocol parameters was necessary to solve the phase problem [2]. The enzyme structure determined in several crystal forms uncovers a new nuclease/DNase fold. Structural analysis, bioinformatic analysis, and activity measurements for the wt and mutant forms of the enzyme led to conclusions regarding the position and composition of the active site. Detailed metal-dependence, stability and cleavage specificity profiles show the necessity of divalent ions for the activity, high temperature stability, and a time-dependent preference for the formation of single strand breaks on dsDNA substrate at sequence-specific sites.

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Keywords: DNase, metal-dependent, X-ray structure

Allosteric coupling between autophosphorylation and phosphorylgroup transfer in a prototypical twocomponent signal transduction system

Ariel Mechaly¹, Pedro Alzari², Jean-Michel Betton², Alejandro Buschiazzo³, Ahmed Haouz¹, Nathalie Sassoon², Silvia Soto-Diaz²

- 1. Plateforme de Cristallographie, Institut Pasteur, Paris, France
- 2. Unite de Microbiologie Structurale, Institut Pasteur, Paris, France
- Laboratory of Molecular and Structural Microbiology, Institut Pasteur de Montevideo, Montevideo, Uruguay

email: ariel.mechaly@pasteur.fr

Prototypical two-component signal transduction systems comprises a sensor histidine kinase (HK) receptor and a response regulator (RR). Input signals induce sensor HK autophosphorylation, and the subsequent transfer of the phosphoryl-group to the RR. Upon receiving the phosphoryl-group, the RR triggers an adaptive response, often at the transcriptional level. To gain insights into how the autokinase and phosphotransferase activities of the sensor HK are coordinated, we solved structures of the catalytic core domains of the prototypical CpxA-CpxR system [1]. Our data suggest a concerted switch -involving large-scale domain motions- by which autophosphorylation and phosphotransfer reactions are allosterically coupled.

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Keywords: Histidine kinase, Response regulator, phosphotrasfer

MS09-P15

Helicobacter pylori urease structures by Cryo-EM and X-ray crystallography

Eva Cunha¹, Xiaorui Chen², Hartmut Luecke¹

- Structural Biology and Drug Discovery Group, Norwegian Centre for Molecular Medicine (NCMM), Nordic EMBL Partnership, University of Oslo, Oslo, Norway
- 2. University of California, Irvine, Irvine, United States of America

email: eva.cunha@ncmm.uio.no

Half the world's population is chronically infected with Helicobacter pylori, causing gastritis, gastric ulcers and being the major risk factor for gastric adenocarcinoma. H. pylori's urease and proton-gated inner-membrane urea channel, HpUreI, are essential for pathogen survival in the acidic environment of the stomach. The channel is closed at neutral pH and opens at acidic pH to allow the rapid access of urea to cytoplasmic urease. Urease produces NH₃ and CO₂, neutralizing entering protons and thus buffering the periplasm to a pH of roughly 6.1 even in gastric juice at a pH near 2. The urease crystal structures show a 1.1 MDa dodecameric assembly composed of two different subunits, α and β , 61.7 kDa and 26.5 kDa, respectively. The dodecamer is arranged in four copies of the trimeric $(\alpha,\beta)_3$ unit, resulting in a tetrahedral complex. Superposition of uninhibited and acetohydroxamic acid-inhibited crystal structures reveals a flap motion of a helix-turn-helix motif at residues $\alpha 313 - \alpha 346$. When the inhibitor is bound, the flap moves outwards, creating an opening to the active site, whereas in the absence of the inhibitor the flap is closed, preventing access to the active site. The recent "resolution revolution" in cryoEM, driven by developments in instrumentation such as direct detectors, coupled with major improvements in data analysis, has put Cryo-EM at the forefront of structural biology for attaining high-resolution models in close-to-native conditions. Since 2015, several records have been achieved with the highest resolution structure reported so far for glutamate dehydrogenase (soluble protein, 1.8 Å), anthrax toxin (membrane protein, 2.9 Å) and hemoglobin (only 64 kDa, 3 Å). We have determined the structure of H. pylori urease using cryo-EM to a resolution of 3.1 Å and we compare it with the previously determined crystal structures.



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Keywords: Helicobacter pylori, Urease, Cryo-EM

MS10- Hydrogen-bonding & weak interactions studied by neutrons and X-rays

Chairs: Prof. Marta E. G. Mosquera, Dr. Matthew Blakeley

MS10-P01

Frequency and hydrogen bonding geometry of nucleobase homodimers in small molecule crystals

Malgorzata Cabaj¹, Paulina Dominiak¹

1. Biological and Chemical Research Centre, Department of Chemistry, University of Warsaw, Warsaw, Poland

email: mcabaj@chem.uw.edu.pl

The issue of various nucleobase pairs and their interactions occurring in RNA and DNA has been already studied from many different perspectives. In this survey, we wanted to approach the subject from more "chemical" point of view and see how nucleobases interact inside crystals. Our study is based on geometric data like bond lengths and bond angles taken from the Cambridge Structural Database (CSD), as well as types of protonation of investigated nucleobase, if the hydrogen positions were available.

We searched for nucleobase homodimers resembling those found in RNA and DNA, which means two nucleobases interacting through at least two hydrogen bonds formed in the molecule plane. The investigated compound were derivatives of adenine, guanine, hypoxanthine, thymine, uracil, and cytosine. We divided our findings into many categories including types of dimers, their protonation and if the N9 or N1 (for purines and pyrimidines respectively) is substituted with only hydrogen or larger substituent that may influence the way the nucleobase forms dimers. In our study, we analyze the various dependencies between the geometry of the molecule and what types of structures it prefers to form. We investigated not only neutral forms of nucleobases, but protonated too, and analyzed how protonation and charge influence the ability of a molecule to form homodimers.

Our study finds that for purines the most active edge is Hoogsten edge, taking part in the formation of dimers found in more than half of the investigated structures. Mixed interactions between the Hoogsteen edge and Watson-Crick edge are also very common, as they allow the molecules to align into infinite ribbons.

For pyrimidines, the situation is much different, as the various possible interactions between Watson-Crick edges of molecules dominate the charts. Only uracil behaves differently from thymine and cytosine, as it eagerly forms trans Watson-Crick - Hoogsten interaction, namely the Calcutta dimer. For all nucleobases, there is a common trend of sugar edge interactions being more frequent if the molecule is substituted with hydrogen in N9 or N1. Fig. 1. Examples of homodimers of adenine and cytosine, with the naming of the edges



Keywords: nucleobases, hydrogen bonding

MS10-P02

Analysis of the hydrogen bonds in the crystal structures of the pyrrole-2-yldichloromethyl ketone derivatives

Małgorzata Domagała¹, Alina T. Dubis¹, Marcin Palusiak¹

1. Faculty of Chemistry, University of Lodz, Lodz, Poland

email: mdomagala@uni.lodz.pl

Pyrroles are both important natural products and crucial starting materials for the synthesis of porphyrins. Nevertheless, a brief survey of the Cambridge Structural Database [1] shows that there are almost 500 instances of the organic structures with a 2-substituted pyrrole core and almost 100 instances with the pyrrol-2-yl carbonyl core. What is more, only a few crystal structures of aromatic N-unsubstituted monopyrroles have been reported. In crystal structures of investigated compounds, we expected the existence of the net of hydrogen and halogen bonding as it was in case of the trichloromethyl derivative of pyrroloketone [2]. However, X-ray structure determinations showed only the latter one. In an extension of ongoing studies on the hydrogen bonding patterns in porphyrins and dipyrromethanes, we were also interested in the strengths and types of hydrogen bonds of isolated pyrrole units. For initial studies we choose 2,2-dichloro-1-(1H-pyrrol-2-yl) ethanone and 2,2-dichloro-1-(1-methyl-1H-pyrrol-2-yl) ethanone. The calculations have been performed using Gaussian03 sets of codes, and by means of the density functional methods (DFT). The H-bonding characteristics of the complexes have been investigated with the use of Bader's theory QTAIM [3].

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Keywords: hydrogen bond, monopyrolle

MS10-P04

Rotational dynamics of methyl ammonium ions and hydrogen-bonding in orthorhombic CH₃NH₃PbI_{2.94}Cl_{0.06} by means of neutron scattering and IR investigations

Götz Schuck¹, Monika Koch-Müller², Ilias Efthimiopoulos², Frederike Lehmann¹, Susan Schorr¹

- Helmholtz-Zentrum Berlin f
 ür Materialien und Energie GmbH, Berlin, Germany)
- 2. Deutsches GeoForschungsZentrum GFZ, Potsdam, Germany

email: goetz.schuck@helmholtz-berlin.de

Perovskites with ABX₃-structure show huge possibilities for element substitution on the A-, B- and X-sites, resulting in a broad variety of physical properties. One field of interest is chlorine-substituted methyl ammonium lead triiodide in which A is the organic unit $[CH_3NH_3]^+ = MA$, $B = Pb^{2+}$ and $X = I_{3-3}CI_3$.

We chose to substitute 2 % of the iodine in MAPbI₃ with chlorine since recent investigations with synchrotron XRD showed that only a narrow range of up to 2.5 % of the iodine in MAPbI₃ can be substituted with chlorine. At the same time, only up to 1 % of the iodine in MAPbCI₃ can be substituted, meaning there is a large miscibility gap. [1]

The aim of the quasi-elastic neutron scattering (QENS) investigations presented here is to understand the interrelationship of the static and the dynamic structure of MAPbX₃ by comparing the temperature-dependent methyl ammonium rotational dynamics of MAPbI3, MAPbI294Cl006 and MAPbCl3. Combining the QENS results with the analysis of temperature-dependent IR vibrational spectra of MAPbI3, MAPbI2.94Cl0.06 and MAPbCl3 helps us understand the influence of the rotational dynamics of the methyl ammonium cation on the hydrogen-bonding layers in the orthorhombic low temperature phase. Recently, the presence of layers with X...H-N hydrogen-bonds in the orthorhombic phase of MAPbX₃ was discussed to explain the drastic changes of MA IR vibrational modes across the tetragonal-orthorhombic phase transition (Fig. 1). The transformation of the 2-dimensional orthorhombic hydrogen-bond layers into a more 3-dimensional arrangement in the tetragonal phase is an important feature, providing deeper insight into the mechanisms that lead to a free-rotating MA molecule in the inorganic host structure. [2]

In recent QENS investigations on MAPbI₃ [3], two quasi-elastic components were identified in the tetragonal (161.5 K < T < 327 K) and cubic (T > 327 K) phase. It was interpreted that, in the cubic and tetragonal phases, the MA ion exhibits four-fold rotational symmetry perpendicular to the C-N axis (C₄) along with three-fold rotation parallel to the C-N axis (C₃), while only C₃ rotation was present in the orthorhombic Pnma phase (T < 161.5 K). [3] Here, we reinvestigate the suggested jump-models for MAPbI₃ and show the validity of the proposed QENS interpretation for MAPbI_{2.94}Cl_{0.06} and MAPbCl₃.



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Keywords: Hybrid Perovskite, Quasielastic Neutron Scattering, Hydrogen-Bonding

MS10-P05

Co-crystal or salt? A cautionary tale when inferring proton disorder solely from X-ray and computational data

George Sackman¹, Richard Cooper¹, Alison Edwards²

- 1. Department of Chemistry, University of Oxford, Oxford, United Kingdom
- 2. Australian Centre for Neutron Scattering, Sydney, Australia

email: george.sackman@chem.ox.ac.uk

The pharmaceutical industry is constantly driven to enhance the physical properties of medicines and active pharmaceutical ingredients (APIs). These improvements can often be achieved by identifying novel solid forms of an API, such as co-crystals and salts.[1]

Co-crystals and salts are distinguished by the degree of proton transfer between an acid and a base in the structure. In a co-crystal, proton transfer does not occur and the proton remains on the acid. While in a salt, proton transfer to the base is complete. However, many materials can exist in an intermediate state along a continuum between co-crystals and salts, where proton transfer is partially complete.[1]

During a recent blind test of crystal structure prediction methods, one of the target structures was a 1:1 co-crystal of 3,5-dinitrobenzoic acid and Tröger's base (3,5-DNBA:TB). It was predicted, using density functional theory calculations, that 3,5-DNBA:TB may exhibit partial proton transfer of the carboxylic acid proton to an amine nitrogen atom of the base.[2]

Following this blind test, X-ray analysis of 3,5-DNBA:TB was performed. This provided supporting evidence for partial proton transfer, by indicating that the proton may be disordered over two sites (with occupancies of 0.58(3) on the carboxylic acid oxygen and 0.42(3) on the amine nitrogen).[3]

In order to study this potential hydrogen disorder, an accurate determination of the hydrogen atom positions was required. Therefore, neutron single crystal diffraction was employed, with Laue diffraction patterns collected at 150K on the KOALA Laue diffractometer at the Australian Centre for Neutron Scattering.

However, the neutron data shows that the proton is not disordered over two sites. The Slant Fourier map shows clear single site occupancy of the hydrogen closer to the carboxyl group (O-H 1.147(8)Å). This demonstrates the need for neutron data to confirm or deny whether a hydrogen is disordered or not.

Further neutron data was collected for a related material where the X-ray data indicated proton disorder: 1:1 3,5-bis(trifluoromethyl)benzoic acid and Tröger's base (3,5-BJTFBA:TB). The neutron data again provided evidence that this proton was in fact not disordered over two sites. Therefore, we recommend that one should be cautious when inferring that a structure contains disordered protons, solely based on X-ray and computational data.



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Keywords: Neutron, Disorder, Hydrogen

MS10-P06

Interactions studies in the crystal structures of Thiosemicarbazones and their Thiazol derivatives

Doaa Ahmed Osman¹, Mohammed S. M. Abdelbaky¹, Rafael Mendoza-Meroño¹, Santiago García-Granda¹

1. Department of Physical and Analytical Chemistry, University of Oviedo, Oviedo, Spain

email: doaaosman90@gmail.com

Thiosemicarbazone compounds have been the subject of intense research for the last twenty years due to their biological and medicinal properties (1). Other interesting application is the possibility of obtaining thiazoles derivatives from thiosemicarbazones using the Hantzsch Reaction; these compounds also present pharmaceutical and biological activities (2). Structurally thiosemicarbazones are versatile building biologs in the synthesis of densely sustituted blocks (3).

In this work we present the crystal structure of some thiosemicarbazones (figure-1a) and their thiazol derivatives (figure-1b), focusing in the study of the interactions that stabilize the crystal lattice.

In general, in the molecular crystals of thiosemicarbazones, hydrogen bonds interactions are established through –NH-C(S)-NH-N= fragment, forming in many cases *synthons*. Even though that C=S···H-N hydrogen bond is weaker than their C=O···H-N analogous, the effective electronegativity of S is increased by conjugative interactions between C=S and the lone pair of one or more N substituyents. This effect is called *resonance-induced hydrogen bonding at Sulfur Acceptor* (4). Due to the low solubility of thiosemicarbazones we use different mixtures of solvents in order to crystallize these compounds. For this reason is possible the inclusion of solvent molecules in the crystal lattice to form the corresponding solvates (5), in these cases we analyze the influence of the solvent in the *synthons* formation.

In thiazol compounds which contain halogen atoms (Cl) and phenyl groups, C-H···Cl and π - π stacking interactions have been also studied.



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Keywords: Thiosemicarbazones, Thiazols, Weak interactions

MS10-P07

Structural studies of cycloheptylamine and alcohols co-crystals

Bernadeta Nowosielska¹, Łukasz Dobrzycki¹, Grzegorz Cichowicz ¹, Roland Boese², Michał Cyrański¹

- 1. Faculty of Chemistry, University of Warsaw, Warsaw, Poland
- 2. Institute of Inorganic Chemistry, University of Duisburg-Essen, Duisburg, Germany

email: bernadeta.nowosielska@student.uw.edu.pl

Cycloheptylamine is a primary amine with aliphatic seven-member ring. The compound is liquid at room temperature and its melting point, according to Jean-Claude Bradley Melting Point Dataset yields 255K. The crystal structure of this amine is not known. Primary amines are capable to co-crystallize with alcohols due to the formation of hydrogen bonds between amino and hydroxyl groups. The common motifs in such systems are ribbons with two different symmetries (-1 and 2_1). The aim of the work was a systematic investigation of the feasibility of the amine cocrystallization with low molecular weight monohydric alcohols. A seven-membered carbon ring with or without a heteroatom is relatively labile, therefore an additional goal of the work was a conformational analysis of this molecular fragment.

The examined mixtures are liquid at room temperature, thus during experiments special approach was necessary. The sample placed in thin-wall glass capillary and cooled was irradiated with focused IR laser beam[1]. This in situ crystallization technique gave sample suitable for single crystal X-ray analysis. However, in most cases obtained phases where oligocrytalline. During experiments, the structures of the neat amine and 12 co-crystals with alcohols were obtained. Interestingly the melting point of the amine is equal to 204K. In all by one of the co-crystals, molecules are arranged in one-dimensional ribbons with hydrogen bonds presents between NH₂ and OH groups. In the co-crystal with methanol, molecules are organized in layers. It was not possible to obtain a co-crystal with tert-butanol, probably due to the large steric hindrance of the aliphatic group of the alcohol. In the majority of the structures the amine ring is disordered.

The seven-member aliphatic ring may exist in many conformations. Therefore the puckering analysis of the obtained structures and those retrieved from the Cambridge Structural Database[2] containing seven-membered rings was performed. Any seven-membered ring can be divided into four orthogonal modes, corresponding to two irreducible representations of incline from the XY plane for the D₇h group[3]. Presentation of the results, in form of a quaternary phase diagram, characteristic for mixtures containing four components, shows that the majority of points are located on the section plane of the tetrahedron, and the deviating ones correspond to structures where the disorder of the ring was probably overseen.

Relatively small variability of the structural motifs in obtained co-crystals can be used to design new systems with the appropriate arrangement of molecules, which, for example, will exhibit photochemical activity.

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Keywords: amines, alcohols, ring-puckering

MS10-P08

A novel salt of antidiabetic drug metformin resulting from a proton transfer reaction: Synthesis, characterization, crystal structure and solution studies

Rafael Mendoza Meroño¹, Fatemeh Ghasemi², Khaled Ghasemi², Ali Reza Rezvani², Ardeshir Shokrollahi³, Masoud Refahi³, Santiago García Granda⁴

- Servicios Científico-Técnicos. University of Oviedo, Oviedo, Spain
- Department of Chemistry, Faculty of Science, University of Sistan and Baluchestan, Zahedan, Iran
- 3. Department of Chemistry, Yasouj University, Yasouj, Iran, Yasouj, Iran
- Departamento de Química Física y Analítica, Universidad de Oviedo–CINN, Oviedo, Spain

email: rafam80@gmail.com

The product of proton transfer reactions between donors and acceptors in which the proton from one species is transferred to the basic center has been designated by different names such as "proton transfer compound" (PTC), "charge transfer complex" (CT-complex) and "H-bonded complex". These are equivalent and merely emphasize different aspects of the same phenomenon. In recent years, the design and development of new active pharmaceutical ingredients (APIs) based on the proton transfer reactions have been widely developed (1). N,N-dimethylbiguanide (known as metformin), is the first line drug of choice to treat non-insulin dependent mellitus, which contains the guanidine moiety that can easily forms strong hydrogen bonds with the acidic functionalities like acids and phenols (2). Metformin can be administered in the form of one of its pharmaceutically acceptable salts of various organic and inorganic acids. As part of our studies on proton transfer compounds and their metal complexes of biological interest, here-in, we report new proton transfer compound, [(MetH2)(HO-dipicH)2·H2O], metformin with 4-hydroxy-2,6-pyridinedicarboxylic acid. The proton transfer compound was synthesized and characterized by FTIR, ¹H and 13C NMR, and single crystal X-ray studies (Fig 1). The solution potentiometric studies provided additional evidences of interaction between HO-dipicH2 and metformin, supporting the results obtained from the solid state studies. We gratefully acknowledge the support of this work by the Sistan and Baluchestan University. Financial support from Spanish Ministerio de Economía y Competitividad (MAT2013-40950-R and MAT2016-78155-C2-1-R), Factoría de Cristalización-Consolider Ingenio 2010).



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Keywords: Proton transfer, X-ray structure.

MS11- Hot structures in biology

Chairs: Prof. Maria Joao Romao, Prof. Fred Antson

MS11-P01

Neanderthal adenylosuccinate lyase: insights in catalysis and link with diseasecausing mutation

Bart Van Laer¹, Ulrike Kapp¹, Montserrat Soler-Lopez¹, Kaja Moczulska², Svante Pääbo², Gordon Leonard¹, Christoph Mueller-Dieckmann¹

- 1. Structural Biology group, European Synchrotron Radiation Facility (ESRF), Grenoble, France
- 2. Max Planck Institute for Evolutionary Anthropology, Leipzig, Germany

email: bart.van-laer@esrf.fr

Adenylosuccinate lyase is a conserved enzyme involved in purine metabolism for which several mutations in the human enzyme (hADSL) are known to affect intelligence and behaviour. During evolution modern humans acquired a specific substitution (Val429Ala) in ADSL distinguishing it from the ancestral variant present in Neanderthals (nAD-SL). I will present a structural, biophysical and biochemical comparison of hADSL and nADSL aimed at determining whether this substitution is functionally relevant and could be responsible for phenotypical differences between these species. This work shows that hADSL and nADSL differ in thermal stability but not in enzymatic activity. Similar observations are made when comparing native hADSL with hADSL containing the nearby disease-causing Arg426His substitution hinting towards a phenotypical effect. In addition the combined X-ray crystallography and SAXS data reveals that ADSL undergoes conformational changes during catalysis which together with the structure of a hitherto undetermined product bound conformation helps explain the effect of several human disease-causing substitutions.

Keywords: Neanderthal, Human disease.

The stucture of human ASCT2 neutral amino acid transporter

Albert Guskov¹, Alisa Garaeva¹, Gert Oostergetel¹, Cornelius Gati², Cristina Paulino¹, Dirk Slotboom¹

- Groningen Biomolecular Sciences and Biotechnology Institute / University of Groningen, Groningen, Netherlands (Holland, Europe)
- Department of Structural Biology / Stanford University, Stanford, United States of America

email: a.guskov@rug.nl

Human ASCT2 belongs to the SLC1 family of secondary transporters and is specific for the transport of small neutral amino acids, including glutamine. ASCT2 is upregulated in cancer cells, and serves as the receptor for many retroviruses, thus it is a potential drug target. I will report a structure of human ASCT2 at 3.85 Å resolution obtained using single particle Cryo-EM. The structure of the functional and unmodified protein sheds light on the transport mechanism of SLC1 members in general, and reveals insight in specific functions of human ASCT2. ASCT2 forms a homotrimeric complex, in which each subunit contains a transport and a scaffold domain. Each of the scaffold domains contains a prominent extracellular extension, which is specific for human ASCT2 and forms the predicted docking site for retroviruses. The transporter adopts an inward-oriented state that resembles the unlocked state of a mutant of prokaryotic homologue GltPh, but in ASCT2 the transport domain is located farther towards the cytoplasmic side of the membrane where it is largely detached from the central scaffold domain. The domain detachment may be required for substrate binding and release on the intracellular side of the membrane. I will also provide a detailed comparison with the previously resolved structures of archaeal homologues of glutamate transporters Glttk and Gltph, as well as human EAAT1 transporter.

Keywords: glutamine transporter, ASCT2, membrane proteins

MS11-P03

Structure and function of proteins involved in targeting of tail-anchored membrane proteins to the membrane of ER or chloroplast

Chwan-Deng Hsiao1, Tai-Wen Lin1, Hsin-Yang Chang2

- 1. Institute of Molecular Biology, Academia Sinica, Taipei, Taiwan
- 2. Department of Marine Biotechnology and Resources, National Sun Yat-sen University, Kaohsiung, Taiwan

email: hsiao@gate.sinica.edu.tw

Nearly 5% of membrane proteins are guided to nuclear, endoplasmic reticulum, mitochondrial, Golgi, or peroxisome membranes by their C-terminal transmembrane domain and are classified as tail-anchored (TA) membrane proteins. During the biosynthesis of TA membrane proteins, their single C-terminal trans-membrane segment is inserted into the ER membrane for orientating the functional domain(s) towards the cytosolic side of the cell. The machinery responsible for this post-translational process has only recently come to light. In yeast, the proteins participating in TA protein insertion was previously identified to be conducted by the GET pathway (Guided Entry of Tail-anchored proteins) including Get1, Get2, Get3, Get4, Get5, Sgt2 and Ybr137wp. In my laboratory, we investigated the interactions between these components from Saccharomyces cerevisiae. Recently, we also determined the crystal structure of arsenite transporter 1 (ArsA1, the homologs of yeast ATPase Get3) from green alga. Our binding activity assay demonstrated that ArsA1 can specifically recognize the transmembrane region of chloroplast TA protein Toc34 but not ER TA protein Sec61β. Based on the ArsA1 structure, we uncover a distinct mechanism for specific filtering between ER and chloroplast TA proteins and successfully manipulate the specificity of mutant ArsA1 for a set of ER TA protein. Our biochemical and structural data provide new insight for the specific selection of ER and chloroplast TA proteins for membrane insertion.

Keywords: tail-anchored membrane protein, mitochondrial, chloroplast

The crystal structure of the CARD-CARD disk of the human apoptosome and its structural insights into the assembly of the death-domain fold

Su-Chang Lin1, Yu-Chih Lo2, Tsung-Wei Su1

- 1. Genomics Research Center, Academia Sinica, Taipei, Taiwan
- 2. Department of Biotechnology and Bioindustry Sciences, National Cheng Kung University, Taipei, Taiwan

email: tomlin@gate.sinica.edu.tw

The caspase recruitment domain (CARD) of the human apoptosome recruits caspase-9 CARD via the homotypic interactions for caspase activation in apoptosis. Here we present the crystal structure of the CARD-CARD disk of the human apoptosome and also show the difference in the CARD assembly between the *Caenorhabditis elegans*, Drosophila, and human apoptosomes, which suggests that the helical assembly only exists in the vertabtate DD-folds. We also found that of the death-domain folds have five different assembling mechanisms for their specific roles in signal transduction.

The CARD-CARD disk of the human apoptosome



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Keywords: Apoptosome, assembly, death domain

MS11-P05

Structure of human natural killer cell receptor NKR-P1 in complex with its ligand LLT1

Tereza Skalova¹, Jan Bláha², Jan Stránský¹, Tomáš Kova¹, Jarmila Dušková¹, Yuguang Zhao³, Karl Harlos³, Ondřej Vaněk², Jan Dohnálek¹

- Institute of Biotechnology CAS, The Czech Academy of Sciences, v.v.i., Průmyslová 595, 252 50 Vestec, Czech Republic
- Department of Biochemistry, Faculty of Science, Charles University, Hlavova 8, 128 40 Prague, Czech Republic
- Division of Structural Biology, The Wellcome Trust Centre for Human Genetics, University of Oxford, Roosevelt Drive, OXFORD OX3 7BN, United Kingdom

email: t.skalova@gmail.com

Natural killer cells are white blood cells able to kill tumor, virus-infected or stressed cells. NKR-P1 is a C-type lectin like-receptor on surface of human natural killer cells and LLT1 is its binding partner belonging to the same structural family.

Recently, we have expressed, purified and solved four crystal structures of the extracellular part of LLT1 in monomeric, dimeric and hexameric form [1, 2]. In this contribution, we present three more structures characterizing this receptor-ligand binding pair: structures of the extracellular part of NKR-P1 in the fully glycosylated and deglycosylated form and a structure of the NKR-P1:LLT1 complex. Expression and purification of NKR-P1 was described by us recently as well [3].

All three crystal structures show NKR-P1 in a dimeric form with an unexpected dimerization mode. Unlike LLT1, which has the α 2 helix in the dimerization interface, NKR-P1 dimer has the α 1 helix in its dimerization interface. This different dimeric arrangement of both proteins enables spatial connection of NKR-P1 with LLT1 not only in a single molecular complex, but in a periodical chain of alternating receptor/ligand molecules. Such chain we really observe in the presented crystal structure.

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Keywords: immune receptor, natural killer cell, protein-protein complex

Structural characterization and functional studies of putative human glutathionespecific γ-glutamylcyclotransferase 2 (ChaC2 enzyme)

Nguyen Thi Kim Yen¹, Byung Woo Han²

- Division of Structural Biology, The Wellcome Trust Centre for Human Genetics, University of Oxford, Roosevelt Drive, OXFORD OX3 7BN, United Kingdom
- 2. Department of Pharmacy, Seoul National University, Seoul, Korea South

email: kimyen@snu.ac.kr

Putative glutathione-specific y-glutamylcyclotransferase 2 (ChaC2) enzyme degrades glutathione which is involved in various signaling pathways and cellular detoxification. To elucidate its catalytic mechanism, we implemented structural biology approaches for ChaC2. Since SeMet-based phasing methods are generally applicable to proteins with at least one methionine per 100 amino acid residues, ChaC2 was a borderline case. We mutated several leucine and isoleucine residues of ChaC2 to methionine residues to enhance the phasing power for multi-wavelength anomalous diffraction (MAD) method and hence structure determination. From structure analysis and alignment with other y-glutamylcyclotransferase, we hypothesized that Glu83 of ChaC2 may play an important role in enzyme activity of ChaC2. We crystallized and obtained the structure of ChaC2 E83Q mutant by molecular replacement method. Excitingly, the structure of this mutant differed from that of the wild type suggesting the vital role of this residue. Our results provide an insight on the effect of a mutation on enzyme activity of ChaC2 and its role in cell. Further experiments need to be performed to elucidate the mechanism of how ChaC2 can cleave specifically on glutathione.



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Keywords: enzyme, Structural Biology, Glutathione

Crystal structure of a mammalian pseudokinase reveals an original dimerization

Gilles Labesse¹ Céline Lecointre², Valérie Simon², Clément Kerneur², Frédéric Allemand ¹, Ingrid Montarras², Muriel Gelin¹, Serge Urbach³, Serge Roche²

- 1. Centre de Biochimie Structurale, CNRS, Montpellier, France
- 2. Centre de Recherche de Biologie cellulaire de Montpellier, CNRS, Montpellier, France
- 3. Institut de Génomique Fonctionnelle, CNRS, Montpellier, France

email: labesse@cbs.cnrs.fr

Although partially or totally devoid of any ATP binding or hydrolysis, pseudokinases are now recognized as key players in cell signaling. However, their functioning is still unclear for a number of such pseudokinases encoded in the mammalian genomes. Here we describe the crystal structure of the folded region of SGK223, a large pseudokinase from rat. We could solve the crystal structure by molecular replacement, at a 3.0 A resolution, despite a low overall sequence identity (20-25% over the whole kinase domain), using the software Phenix, an ensemble of partial models built using our server @TOME-2 and data recorded automatically on the beamline MASSIF-1 at the ESRF synchrotron.

The structure contains a classical protein kinase fold, devoid of any ATP-binding activity. It also highlighted several sequence motifs conserved in other psudokinases and extend the corresponding superfamily. Interestingly, these pseudokinases possess N- and C-terminal extensions forming an original dimerization domain. This dimeric pseudokinases have been linked to cancer by up-regulating protein tyrosine phosphorylation. Our results suggest a structural model for understanding how pseudokinases induce protein tyrosine phosphorylation [1,2].



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Keywords: cell signaling, cancer, protein-kinase

MS11-P08

Structure and function of DJ-1 superfamily proteins from staphylococcus aureus

Ae-Ran Kwon1, Hyo Jung Kim2

- 1. College of Herbal Bio-Industry, Daegu Haany University, Gyeongsan-City, Korea South
- 2. School of Pharmacy, University of Nottingham, Nottingham, United Kingdom

email: arkwon@dhu.ac.kr

The DJ-1/ThiJ/PfpI superfamily of proteins is highly conserved across all biological kingdoms showing divergent multifunctions, such as chaperone, catalase, protease, and kinase. The common theme of these functions is responding to and managing various cellular stresses. Most members of the DJ-1/ThiJ/Pf pI superfamily are oligomers and are classified into subfamilies depending on discriminating quaternary structures (DJ-1, YhbO and Hsp types).

SAV1875, a conserved protein from Staphylococcus aureus, is a member of the YhbO-type subfamily. The crystal structure of SAV1875 from S. aureus was determined. The cysteine residue located in the dimeric interface (Cys105) forms a catalytic triad with His106 and Asp77, and it is spontaneously oxidized to Cys105-SO₂H in the crystal structure. To study the oxidative propensity of Cys105 and the corresponding functional differences with changes in cysteine oxidation state, the crystal structures of SAV1875 variants E17N, E17D and C105D, and over-oxidized SAV1875 were determined. We identified SAV1875 as a novel member of the YhbO-type subfamily exhibiting chaperone function. However, if SAV1875 is over-oxidized further with H₂O₂, its chaperone activity is eliminated. On the basis of our study, we suggest that SAV1875 functions as a chaperone and the redox state of Cys105 may play an important role.

The Hsp-type subfamily includes Hsp31, a chaperone and glyoxalase III. SAV0551, an Hsp-type subfamily member from Staphylococcus aureus, is a hypothetical protein that is predicted as Hsp31. Thus, to reveal the function and reaction mechanism of SAV0551, the crystal structure of SAV0551 was determined. We have shown that SAV0551 functions as a chaperone and that the surface structure is crucial for holding unfolded substrates. As many DJ-1/ ThiJ/PfpI superfamily proteins have been characterized as glyoxalase III, our study also demonstrates SAV0551 as a glyoxalase III that is independent of any cofactors. We have confirmed that the components required for reaction are present in the structure, including a catalytic triad for a catalytic action, His78 as a base, and a water molecule for hydrolysis. Our functional studies based on the crystal structures of native and glyoxylate-bound SAV0551 will provide a better understanding of the reaction mechanism of a chaperone and glyoxalase III.

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Keywords: DJ-1/ThiJ/PfpI superfamily, Staphylococcus aureus

DPP8 and DPP9 structure, mechanism and interaction with SUMO1

Breyan Ross¹, Stephan Krapp², Ruth Geiss-Friedlander³, Robert Hube¹

- 1. Max Planck Institute of Biochemistry, Planegg, Germany
- 2. Proteros Biostructure GmbH, Planegg, Germany
- Institute of Molecular Biology, Göttingen University, Göttingen, Germany

email: ross@biochem.mpg.de

Cells require specific molecular entities to regulate biological processes, which are often out of balance in diseases. Once these entities are identified, their activities may be modulated by specific ligands. DPP4 protein is an example of a target to successfully treat type II diabetes by small molecule ligands [1]. Other members of the DPP4 family are similarly interesting. DPP8 and DPP9, are active serine proteases located inside cells. They are relevant in immune response and cancer [2]. It is crucial to understand their structures, enzymatic mechanisms and interactions to enable structure-based drug development. DPP8 and DPP9 activity can be modulated by inhibitors like SLRFLYEG, 1G244, and Val-BoroPro. SLRFLYEG is a specific peptidic DPP8 and DPP9 inhibitor with allosteric properties. This inhibitor was designed using a segment of SUMO1. 1G244 is a strong specific competitive inhibitor of DPP8 and DPP9. Val-BoroPro is a non-specific covalent inhibitor of DPP4, DPP8 and DPP9. Regarding binding partners, SUMO1 has been described to form complex with either DPP8 or DPP9 during pulldown experiments using SUMO1-tagged beads. While the complexes are not stable in solution this binding may regulate important signaling in cells.

We hereby reveal DPP8 and DPP9 molecular structures and substrate binding features. Moreover, we clarify how structural differences in inhibitor binding lead to differences in potency and binding mechanisms. DPP8 and DPP9 are structurally related to DPP4, with a conserved α -hydrolase domain and β-propeller domain. However, the mechanism underlying the enzymatic activity differs significantly. We observed a disorder-order transition of a 26 aa segment upon substrate binding. This segment partially folds into an α -helix, which is required to fix the incoming substrate, allowing enzyme activity [3]. Furthermore, we characterize the SUMO1-DPP9 complex using protein-protein interaction assays. We observed a stable complex between DPP9 and oligomeric forms of SUMO1. Therefore, a bis-sumoylated substrate might be the minimal requirement for interaction in a physiological context. The determination of DPP8 and DPP9 crystallographic structures as well as their interaction with SUMO1 can be of paramount relevance in immunological regulation or drug design when treating diseases like cancer.

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Keywords: DPP8, DPP9, SUMO1

MS12- Structural bioinformatics

Chairs: Claudia Lucía Millán Nebot, Dr. Daniel Rigden

MS12-P01

Revealing the properties of small local folds with ALEPH: from structure annotation to *ab initio* phasing

Ana del Rocío Medina Bernal¹, Massimo D. Sammito², Claudia L. Millán¹, Rafael J. Borges³, Isabel Usón⁴

- 1. Structural Biology Unit, Molecular Biology Institude of Barcelona, Barcelona, Spain
- 2. Cambridge Institute for Medical Research, Cambridge, United Kingdom
- Dept. of Physics and Biophysics, Biosciences Institute (IBB), São Paulo State University (UNESP), Botucatu, Brazil
- 4. Structural Biology Unit, Catalan Institution for Research and Advanced Studies (ICREA), Barcelona, Spain

email: ambcri@ibmb.csic.es

Software for structure annotation has become a key aspect for any functional study, as structure is highly conserved and a vast amount of structural data is available. Implemented in software like DSSP, Cablam or Gesamt, algorithms employed for structure analysis are based either on sequence features, geometrical parameters or a combination of them. For the validation context, algorithms based on geometry descriptors have been developed, such as C-Alpha Based Low-resolution Annotation Method (CABLAM)[1]. ALEPH addresses two challenges:

- Revealing structure properties of small local folds, of immediate application to produce models for *ab initio* phasing.
- Flexibly tuning the annotation to the purpose for which it will be used.

ALEPH, which incorporates the previous algorithm Borges [2], has been developed to analyze small local folds. ALEPH is integrated in the ARCIMBOLDO software for ab initio phasing, especially in ARCIMBOLDO SHREDDER [3] for identification of compact folds. The software uses ad hoc parameters called Characteristic Vectors (CV's) for retrieving tridimensional properties of the main chain. CV's exploit the fact that carbonyl oxygens are differently oriented for each secondary structure. Properties of the CV such as their modulus or direction, the angles between them or the distances that separates them, allow to identify different secondary structures and describe their environment. Recent developments, including an increase in the number of parameters used for main chain description and the addition of new mathematical algorithms has allowed not only to improve the precision in the annotation but also its flexibility.

Beyond secondary structure annotation, ALEPH can also optimally superpose very small structures, annotate and extract folds from a model or generate libraries of a given fold. A general description of the performance of ALEPH for validation of non ideal main chains, identification of a fold from an unknown solution and identification of compact structural folds in the frame of ARCIMBOLDO_SHRED-DER will be illustrated.

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Keywords: secondary structure annotation, geometry, phasing



Overcoming phasing difficulties in coiled-coils with ARCIMBOLDO_LITE: verifying solutions

Iracema Caballero Muñoz¹, Massimo Sammito¹, Claudia Millán¹, Nicolas Soler¹, Andrey Lebedev², Isabel Usón¹

- Structural Biology Unit, Institute of Molecular Biology of Barcelona (IBMB–CSIC), Barcelona, Spain
- CCP4, STFC Rutherford Appleton Laboratory, Research Complex at Harwell, Oxford, Great Britain

email: icmcri@ibmb.csic.es

ARCIMBOLDO_LITE is an *ab initio* phasing approach that combines location of small, very accurate model fragments with PHASER followed by density modification and main chain autotracing with SHELXE. Mainly helical structures are favorable cases for this approach, as ideal polyalanine α -helices constitute an excellent approximation of helices in real structures. Coiled coil structures, despite being highly helical, typically present intrinsic difficulties for phasing.

In general, for all coiled coils structures, it can be complicated to distinguish whether prominent features in the Patterson function are due to genuine tNCS or to the intrinsic periodicity of the helix. In addition, often mistranslated solutions reach high scores. This can lead to elimination of all starting hypotheses through the packing filters. At low resolution (2-3Å), the placement of helices occasionally takes place in the correct position but in reversed direction. Also, even when having a correct substructure placed, autotracing the helices from a very partial solution in a map degraded by severe anisotropy, modulation and limited resolution is challenging. And finally, after tracing, the discrimination of correct from the incorrect solutions can be misleading, requiring a final verification step. To overcome these difficulties ARCIMBOLDO_LITE [1] incorporates a set of improvements gathered under a specific coiled coil mode, exploiting new improvements in PHASER [2] and SHELXE [3].

These features were designed for solving coiled coils at resolutions up to 3Å and tested on a pool of 150 structures, showing a 93% success rate. Furthermore, this implementation has allowed to solve new previously unknown structures, and unequivocally identifies correct solutions through the new verification strategy. This idea opens promising perspectives to extend its application within the use of small general model fragments.

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Keywords: ARCIMBOLDO, coiled coils, phasing

MS12-P03

HAR-ELMO: a new quantum mechanicsbased method to refine crystallographic structures of proteins

Alessandro Genoni¹, Lorraine Andrade Malaspina² Benjamin Meyer¹, Simon Grabowsky²

- 1. CNRS & University of Lorraine, Laboratory of Theoretical Physics and Chemistry, Metz, France
- 2. University of Bremen, Institute of Inorganic Chemistry and Crystallography, Bremen, Germany

email: Alessandro.Genoni@univ-lorraine.fr

Nowadays, due to impressive advances from the technological and experimental points of view, sub-atomic and ultra-high resolution X-ray datasets of macromolecules started appearing and their number will certainly increase in the next few years. This makes the refinement of crystallographic structures of biological systems a more and more crucial and difficult challenge, with the need of developing novel refinement techniques able to fully exploit the information content of the new high-resolution X-ray datasets and, consequently, to get unprecedented structural and electron density details of biological molecules.

In this context, an emerging technique of crystallography that can be promisingly used is the Hirshfeld Atom Refinement (HAR). This is a quantum mechanics-based method that, although using only X-ray diffraction data, allows to determine the hydrogen atoms positions with the same precision and accuracy usually attained through neutron diffraction measurements, even when resolution is as low as 0.8-0.9 Å [1]. This would obviously make HAR the perfect strategy to fully exploit the new high-resolution X-ray datasets of macromolecules. Nevertheless, its straightforward application to large systems is actually prevented by the fact that, at each iteration, it requires a tailor-made quantum mechanical calculation, whose computational cost increases with the size of the systems under exam.

The only possibility to overcome this drawback is to couple HAR with quantum mechanics-based linear scaling techniques and, to this purpose, we have recently decided to include the novel libraries of Extremely Localized Molecular Orbitals (ELMOs) [2,3] into HAR. In fact, ELMOs are orbitals strictly localized on small molecular units (e.g., atoms, bonds or functional groups) and, for this reason, easily transferable from a molecule to another [2,3]. Therefore, following a sort of LEGO approach, databanks of ELMOs have been recently constructed. These libraries currently cover all the possible fragments of the twenty natural amino acids and really allow instantaneous reconstructions of wave functions and electron densities of systems ranging from small polypeptides to very large proteins, thus also giving the possibility of computing a large variety of properties for the investigated molecules.

Here, after briefly illustrating the main capabilities of the new ELMO-libraries and of the associated program for the automatic transfer of ELMOs, we will discuss in detail the coupling of these databanks with HAR and we will show recently obtained results that encourage to further improve the technique, with the final goal of making it a powerful routine-strategy for the refinement of macromolecular crystallographic structures. References:

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Keywords: Protein strucures refinement, Hirshfeld Atom Refinement, Extremely Localized Molecular Orbitals

MS12-P04

Identifying amyloid and partially amyloid structures from the protein data bank

Vince Grolmusz1, Kristóf Takács1, Bálint Varga1

1. Eötvös University, PIT Bioinformatics Group, Budapest, Hungary

email: grolmusz@pitgroup.org

The Protein Data Bank (PDB) contains 135 000 entries today. From these, relatively few amyloid structures can be identified, since amyloids are insoluble in water. Therefore, mostly solid state NMR-recorded amyloid structures are deposited in the PDB. Based on the geometric analysis of these deposited structures we have prepared an automatically updated webserver, which generates the list of the deposited amyloid structures, and, additionally, those X-ray crystallography identifyid globular protein entries, which have amyloid-like substructures of a given size and characteristics. We have found that applying only the properly chosen geometric conditions, it is possible to identify the deposited amyloid structures, and a number of globular proteins with amyloid-like substructures. We have analyzed these globular proteins and have found that most of them are known to form amyloids more easily than many other globular proteins. Our results relate to the method of [1], who have applied a hybrid textual-search and geometric approach for finding amyloids in the PDB.

If one intends to identify a subset of the PDB for some applications, the identification algorithm needs to be re-run periodically, since in 2017, on the average, every day 30 new entries were deposited in the data bank. Our webserver is updated regularly and automatically, and the identified amyloid- and partial amyloid structures can be viewed online or their list can be downloaded from the site https:// pitgroup.org/amyloid.

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1, Stanković, I. et al. (2017): Construction of Amyloid PDB Files Database. Transactions on Internet Research. 13 (1): 47-51.

Keywords: PDB, amyloids, webserver

MS12-P05

Coordination of structural bioinformatics activities across Europe

Bohdan Schneider¹, Christine Orengo², Torsten Schwede³, Joel L. Sussman⁴, Janet M. Thornton⁵, Sameer Velankar⁵, Shoshana Wodak⁶

- Laboratory of Biomolecular Recognition, Institute of Biotechnology of the Czech Academy of Sciences, Vestec, Czech Republic
- 2. University College London, London, United Kingdom
- 3. Biozentrum, University of Basel, Basel, Switzerland
- 4. Dept. of Structural Biology, Weizmann Institute of Science, Rehovot, Israel
- 5, European Molecular Biology Laboratory, European Bioinformatics Institutes, Hinxton, United Kingdom
- 6. VIB-VUB Center for Structural Biology, Brussels, Belgium

email: bohdan.schneider@gmail.com

Structural bioinformatics has a broad impact across the life sciences and provides tools to archive, present, analyse, annotate, and predict molecular structures. The science of structural bioinformatics is traditionally very strong in Europe offering many software tools, methodologies, and databases, as well as community-wide prediction challenges. Its applications cover research activities from structural biology to drug discovery and personalized medicine that are all well represented within the national ELIXIR nodes. We believe that the coordination of the many concurrent activities will help to unite the voice of structural bioinformaticians in Europe and thus maximize the impact of structural bioinformatics to the benefit of all researchers in the field and the scientific community at large.

We therefore propose the establishment of an ELIXIR Community in Structural Bioinformatics to represent the broad group of activities in this field. We suggest calling it 3DBio-Info. We volunteer to act as an interim executive committee to organise a kick-off workshop for this Community, which would take place in the Fall of 2018. We will also establish an interim Steering Committee with a structural bioinformatics representative from each ELIXIR node to make sure we capture the interests and activities in each country. Researchers at the kick-off workshop will formulate the goals of the 3DBioInfo Community and collect ideas for Community activities to form the basis of a formal application to the ELIXIR Heads of Nodes.

Keywords: bioinformatics, molecular structure, ELIXIR

MS12-P06

Bringing together functional annotations related to structure

Lukas Pravda1, Sameer Velankar1

1. PDBe, EMBL-EBI, Cambridge, United Kingdom

email: lpravda@ebi.ac.uk

In order to understand macromolecular structures archived in the Protein Data Bank (PDB), it is essential to take into consideration the biological context of these molecules. Multiple specialised resources each provide one or more aspects of the biological context, but it takes significant effort to collect and compare all the information that may be relevant to a specific structure.

PDBe-KB (Protein Data Bank in Europe - Knowledge Base) is a new community driven resource under development by PDBe, which will provide functional annotations for structural data that can be used by the scientific community to answer biological questions. PDBe-KB is a collaborative effort between PDBe and a diverse group of biological resources and structural bioinformatics research teams. This new resource will consolidate older services, such as SIFTS, which focuses on providing seamless mappings between PDB entries and other databases, and data from multiple data enrichment projects. These include the FunPDBe project, which aims to collect and distribute highly enriched, valuable annotations that create a comprehensive biological context for structural models, effectively bringing structure to biology.



Keywords: Protein Data Bank, Functional annotation, PDBe-KB

MS12-P07

Conservation and Variability in Hydrogen Bonding in Proteins

Matthew Merski¹, Jakub Skrzeczkowski¹, Maria W. Górna¹

1. Biological and Chemical Research Centre, Department of Chemistry, University of Warsaw, Warsaw, Poland

email: merski@gmail.com

Hydrogen bonds are an essential part of the structure and function of proteins, defining the secondary structure and the overall fold of the protein as well as being important components of the active sites of enzymes. However, despite the widespread belief that proteins are evolved to sustain a single, folded structure, there is significant, empirically demonstrable variability in the hydrogen bonding pattern of proteins, even within sets of identical protein structures in which there is little overall structural variation. Hydrogen bond variability has been recently clearly demonstrated in a set of structures of a single protein bound to a homologous series of ligands[1]. However, neither the extent of this variability, nor its function has been widely otherwise remarked upon in the current literature. We catalogue the variability of hydrogen bonding patterns in all currently publically known protein structures present in the Protein Data Bank[2]. We use a geometric definition of hydrogen bonding in proteins to focus on the kind of data available from x-ray structures of proteins. We compared the hydrogen bonding pattern between all instances of identical or nearly identical proteins (≥ 90 % sequence identity) which have been deposited at least 10 times in the PDB ($n \sim 6500$) and used this redundancy to measure the inherent variability in a given hydrogen bond. This geometric definition will allow treatment of both strong (e.g. OH-O, NH-O) and weak/ non-traditional (e.g. CH-O, NH-π, OH/NH-S, etc.) protein hydrogen bonds. Identification and characterization of this variability will help to understand the role of this variability in protein structure and also aid in future protein engineering and design efforts.

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Keywords: hydrogen bond, protein

MS13- New insights on diffraction studies of minerals and related materials

Chairs: Dr. Catherine Dejoie Prof. Giuseppe Cruciani

MS13-P01

Crystal chemical features in the row of phosphates and vanadates with alkaline and transition metals

Galina Kiriukhina1, Olga Yakubovich1

 Department of Crystallography, Lomonosov Moscow State University, Moscow, Russia

email: g-biralo@yandex.ru

New crystals were synthesized under hydrothermal conditions, simulating natural middle-temperature hydrothermal zones (T = 230-280 °C; P = 70-100 atm) using complex vanadate/phosphate systems with transition M = Mn, Co, Ni, Cu and alkaline cations A = Na, K, Rb, or NH₄, and Cl⁻, F⁻, CO₃²⁻ mineralizers. The X-ray spectral analysis (JEOL SEM with EDS) provided the chemical composition of the crystals. The crystal structures were determined by single-crystal X-ray diffraction (XCalibur-S-CCD diffractometer). Most of new compounds were found out to be new synthetic modifications of minerals alluaudite KCuMn₃(VO₄)₃, niahite NH₄MnPO₄×H₂O, mahnertite K2.5Cu5Cl(PO4)4(OH)0.5(VO2) H2O, phosphoellenbergerite Na_{0.91}Co₆[HPO₄][H_{0.36}PO₄](OH)₃, elpasolite Rb₂NaAlF₆, and $(NH_4)_2[(V,P)_2O_6]$ with pyroxene structure type; others are «mineralogically probable» phosphates RbCuAl(PO₄)₂, $Na_2Ni_3(OH)_2(PO_4)_2$, $Rb_2Mn_3(H_2O)_2[P_2O_7]_2$, $(Al,V)_4(P_4O_{12})_3$. In accordance with Sandomirsky-Belov principles [1], applied to classification of phosphates with amphoteric oxo-complexes [2], the crystal chemical function of amphoteric metal atoms in all new structures was revealed [3]. In five crystal structures the octahedral complexes of amphoteric metals in the lowest oxidation state build the cationic

part of the structure, forming structure fragments of different dimensionality. These are isolated 0D (Al,V)O₆ polyhedra in tetraphosphate (Al,V)₄(P₄O₁₂)₃. 1D columns of MnO₆ octahedra in diphosphate Rb₂Mn₃(H₂O)₂[P₂O₇]₂. 2D layers of MnO₆, or NiO₆ octahedra in new polymorphic modification of niachite NH₄MnPO₄ :H₂O and Na₂Ni₃(OH)₂(PO₄)₂, respectively, and 3D framework of CoO₆ octahedra in synthetic phosphohellenebergerite Na_{0.91}Co₆[HPO₄][H_{0.36}PO₄](OH)₃.

In the compounds containing several types of amphoteric metals, its coordination environment and crystal chemical function depends on electronegativity. Thus, in the Rb-Cu[Al(PO₄)₂] structure the mixed-type anion framework is built of the AlO₅ and PO₄ polyhedra, while the columns of CuO₆ octahedra form the cationic part of the structure. The main fragment of the alluaudite KCuMn₃(VO₄)₃ structure is the cationic framework of MnO₆ octahedra and flat CuO₄ groups, which is reinforced with anionic VO₄ orthotetrahedra.

In the vanadyl-phosphate analogue of mahnertite $K_{2,5}Cu_5Cl(PO_4)_4(OH)_{0,5}(VO_2) \cdot H_2O$, the copper and vanadi-

um operate as anion formers and build the anionic framework of mixed type together with PO_4 tetrahedra. The anion-forming function of amphoteric vanadium is also established in the structure of vanadate analogue of pyroxene (NH₄)₂[(V,P)₂O₆].

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Keywords: Transition metal phosphates and vanadates, amphoteric oxo-complexes

New borates with similar structures and different properties – acentric nonlinear optical KGd[B₆O₁₀(OH)₂] and centrosymmetric KH0[B₆O₁₀(OH)₂]

Anastasiia Topnikova¹, Elena Belokoneva¹, Olga Dimitrova¹, Anatoliy Volkov¹, Sergey Stefanovich²

- Department of Crystallography, Geological Faculty, Lomonosov Moscow State University, Moscow, Russia
- Department of Chemical Technology and New Materials, Chemical Faculty, Lomonosov Moscow State University, Moscow, Russia

email: nastya_zorina@rambler.ru

Single crystals of two new borates, KGd[B₆O₁₀(OH)₂] and KHo[B6O10(OH)2] [1], have been synthesized under hydrothermal conditions in complicate borosilicate and borate systems at different pH-values. The syntheses were performed at the temperature 270-290 °C under pressure of 70-100 atm. Both structures are similar in unit cell but differ in symmetry. The first borate is found to be acentric (sp.gr. P-62m), the second is centrosymmetric (sp.gr. P-31m) (Fig.1). The same anionic radical of new type in both borates is characterized as polyborate layer composed of tetrahedrons (T) in a form of mica-like layer added by triangles (Δ). Crystal chemical formula of new layer is [B₆O₁₀(OH)₂]⁴- because B2-triangles hold statistically only two positions attributable to the four tetrahedra, notation is $6:[4T + 2\Delta]_{max}$ or three on a ring of six tetrahedra, $[6T + 3\Delta]_{acc}$. Multiplication of the layers by symmetry is differently produced in the structures: by mirror plane in K. Gd-borate or the inversion center in K. Ho-borate. Two polar layers are attached to top and bottom of GdO₆ trigonal prisms and HoO6 octahedrons, correspondingly. K- and B-triangles positions are statistically occupied in both structures. Disorder along c* in acentric KGd[B₆O₁₀(OH)₂] and overlapping of K- and B2-positions in its interlayer space may be eliminated in larger cell with tripled period along c-axis and resulting polar structure of P31 symmetry. In centrosymmetric KHo[B6O10(OH)2], which also has disorder along c* axes and tripling of cell, K- and B2-positions holds the inversion center symmetry. Despite of the almost complete structural identity, new acentric K, Gd-borate clearly demonstrates second-order nonlinear optical activity (SHG response up to 45 SiO₂ units) in contrast to centrosymmetric K, Ho-borate. We suppose that key of properties explanation is in the acentric structure of K, Gd-borate and polar ordering in this crystal.

The reported study was funded by RFBR according to the research project N_{0} 18-35-00645.



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Keywords: structures, borates, symmetry

Structural investigation of the phase transition in the 18-carat gold alloy starting from the disordered state

Imene Lamiri¹, Mohammed S.M. Abdelbaky¹, Santiago García Granda¹, Djamel Hamana²

Physica y Analitica Chimica, Oviedo, Spain
 Physics, Constantine, Algeria

email: imene.lamiri@umc.edu.dz

Phase transition sequences in gold alloys haveattract a lot of interest at the first half of the 20Th century. Where, till now the thorough sequences ant the temperatures are not investigated. The knowing of such precise temperatures and sequences is of high importance according to the gold alloys industrial use [1-3]. Herein, In-situ temperature XRD and mechanical spectroscopy were applied to study phase transitions in AuCu alloy. The phase transition sequences, with the disorder as starting state for the thermal cycle, was investigated upon heating and cooling using heating rate of 1K/min. The sequences of phase transitions recorded show an important succession at continuous heating and subsequent cooling. The transition temperatures were thoroughly determined. This transition sequences determine temperature dependency of elastic and anelastic properties. The mechanical spectroscopy using forced torsion pendulum shows twin boundaries peak as typical peak of the orthorhombic phase AuCuII and transient peak with the onset of the tetragonal AuCuI in A1 phase with the classical Zener peak.

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Keywords: Gold alloys, in-situ temperature XRD, mechanical spectroscopy

MS13-P04

New insights into Eugsterite's structure from SC-ED and PXRD data

Cristobal Verdugo-Escamilla¹, Stef Smeets², Joaquín Criado-Reyes¹, M. O. Cichocka², Duane Choquesillo-Lazarte¹, Fermín Otálora¹, Juan Manuel García-Ruíz¹

- 1. Laboratorio de Estudios Cristalográficos, IACT, CSIC-UGR, Granada, Spain
- Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden

email: cristobal.verdugo@csic.es

Eugsterite is a mineral commonly associated with halite, thenardite, bloedite, gypsum, glauberite and nesquehonite and occurs in some parts of Kenya and in the Konya Basin in Turkey Its crystal structure is unknown and the only information is a list of d spacings and intensities obtained from an X-ray powder pattern of an impure synthetic sample (Vergouwen, 1981).

In this work, we have confirmed the difficulty on purifying eugsterite, reason because the structure solution had to be attempted from Single Crystal Electron Diffraction (SCED) data of a multiphasic sample where only single crystals of eugsterite were measured with the continuous rotation method (Wang *et al.*, 2017).

The structural model obtained from the SCED data was lately used to refine this structure through a Powder X-ray Diffraction (PXRD) dataset of an impure sample containing gypsum, halite and thenardite in addition to eugsterite.

The structure of Eugsterite consists of two crystallographically independent CaNa(SO₄) layers along the *xy*-plane. One layer can be described by two linked columns of NaO₆ polyhedra interconnected via cornersharing SO₄ tetrahedra. The other layer is described as columns formed by face-sharing NaO₆ polyhedra in trigonal antiprismatic arrangement interconnected via cornersharing SO₄ tetrahedron. The layers are interlinked via columns of edge-sharing CaO₈ polyhedra.



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Keywords: Eugsterite, mineral, PXRD

Spatial displacement of forward-diffracted X-ray beams by perfect crystals. Cases: Laue and Bragg geometry

Angel Rodriguez Fernandez¹, Vincent Esposito² Kenneth D. Finkelstein³, Urs Staub², Sven Reiche², Daniel Grolimund², Dario F. Sanchez², Pavle Juranie², Bill Pedrini²

- 1. Imaging MAX IV, Lund, Sweden
- 2. Paul Scherrer Institute, Villigen, Switzerland
- 3. Cornell High Energy Synchrotron Source, Ithaca, United States of America

email: angel.rodriguez_fernandez@maxiv.lu.se

Hard X-ray free-electron lasers (XFELs) are novel photon sources, which rely on the self-amplified spontaneous emission (SASE) process to obtain peak brightnesses in the soft and hard X-ray regime that are orders of magnitude larger than those achieved with insertion devices at third-generation synchrotron light sources. The SASE radiation arises from amplification of stochastic noise in the electron bunch. Therefore, it consists of many longitudinal modes, and exhibits strong shot-to-shot fluctuations of both the mean pulse energy and the pulse spectrum, showing relative bandwidth typically of the order of 10-3. Self-seeding has been proposed as an intensity-efficient mode of operation for XFELs [1]. After SASE amplification in a first undulator section, the electron bunch is separated from the photons and delayed by a magnetic chicane, which also refreshes the electron bunch by suppressing the microbunching that results from the SASE process. The XFEL pulse thus obtained is characterized by the same narrow bandwidth and by a stable wavelength set by the monochromator.

In the hard X-ray regime, monochromators are typically based on perfect crystals. Geloni *et al.* [1] have proposed generating the narrow-band seed with a thin crystal in the Bragg condition. This process of forward Bragg diffraction (FBD) is described by the <u>dynamical diffraction</u> theory presented for spatiotemporal effects by Shvydko [2], which accounts for multiple-scattering effects relevant in perfect crystals. For most of the radiation in the incoming SASE pulse the crystal is transparent. Only the wavelengths that are close to or satisfy the Bragg condition are affected, and a series of time-delayed pulses of low intensity but narrow bandwidth, called echoes, are generated in the temporal tail of the transmitted pulse [1,2].

The work presented here aims to gain a better understanding of space-, time- and frequency-domain effects in the FBD process. The results reported represent the first direct and unambiguous experimental evidence of the spatially displaced echoes in the forward transmitted photon beam, made possible using an X-ray beam focused down to the micrometer scale. Our results are backed up by simulations that confirm the interpretation of the experimental signals in terms of FBD echoes [3]. Fig. 1 shows results obtained from an energy scan at 12 keV with a 400 um thick diamond single crystal with orientation (110) set to diffract at the (220) reflection in Bragg Geometry.



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Keywords: Forward Diffraction, femtosecond, multiplescattering

Measurement of relaxation-free stress profiles in aluminium by multireflection grazing incidence X-ray diffraction with different wavelengths

Victor Righetti1, Tiago Campo1, Lucas Robatto2, Gilmar Thim1

- 1, Laboratório de Plasmas e Processos Instituto Tecnológico de Aeronáutica, São José dos Campos, Brazil
- 2. Centro de Competência em Manufatura Instituto Tecnológico de Aeronáutica, São José dos Campos, Brazil

email: forarodas@gmail.com

The state of residual stresses is of fundamental importance to the mechanical properties of many metals. Resulting properties are function of not only surface, but also the subsurface stress state, usually beyond the penetration depth of most X-ray sources. To circumvent this limitation conventional methods of stress profiling relies on some kind of material removal such as electropolishing or acid polishing, which are known to cause stress relaxation [1], compromising the reliability of such profiles.

Multireflection grazing incidence X-ray diffraction (MGIXD) geometry is seen as an alternative for obtaining relaxation-free, nondestructive residual stress profiles [2], potentially resulting in major revisions of the understanding of subsurface stress influence in metals' mechanical properties.

We discuss here the application of the MGIXD geometry for stress profiling in aeronautical aluminium. In this study a PANalytical Empyrean diffractometer equipped with conventional (Cu) and hard (Ag) sources was used to obtain residual stress profiles of shot peened 7050 aeronautical aluminium in depths up to 200 µm. With this results, comparisons with conventional (destructive) stress profiling methods was also made possible.

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Keywords: residual stress, MGIXD

MS13-P07

Intergrowth of new phosphorus nitride oxide high-pressure phases elucidated using synchrotron radiation

Oliver Oeckler¹, Daniel Günther¹, Dominik Baumann² Philipp Urban¹, Peter Schultz¹, Lukas Neudert², Wolfgang Schnick²

- 1. Faculty of Chemistry and Mineralogy, Leipzig University, Leipzig, Germany
- 2. Department of Chemistry, University of Munich (LMU), Munich, Germany

email: oliver.oeckler@gmx.de

Whereas silicates are among the most thoroughly investigated classes of compounds, much less is known about the closely related oxonitridophosphates and phosphorus oxide nitrides. Different O/N ratios and flexible bonding to N atoms enable a rich structural chemistry, further enhanced by the possibility of including H atoms. Yet, access to new compounds in the system P/O/N/(H) is difficult and often involves high pressure and high temperature. Starting from amorphous phosphorus imide nitride oxide, various SiO2like modifications of PON can be obtained. Yet, syntheses at 1400 °C and up to 16 GPa yielded microcrystalline samples with complex diffraction patterns. Powder diffraction patterns being inconclusive, first information was obtained by electron diffraction and suitable crystallites of new compounds could be identified. Microfocused synchrotron radiation (ID11, ESRF, Grenoble) enables unique insight into the crystal chemistry of such compounds with unprecedented accuracy. Diffraction data from intergrown micrometer-sized crystallites correspond to the superposition of diffraction patterns of H₃P₈O₈N₉ [1] and new phosphorus oxide nitrides.

The compound with the idealized formula P74O59N84 (monoclinic, C2, $V = 4878 \text{ Å}^3$) exhibits a 3D network of P(O,N)₄ tetrahedra, some sharing three vertices. P40O31N46 (monoclinic, C2, V = 2651 Å³) contains similar building blocks and exhibits a higher degree of disorder. Both compounds contain a motif that is similar to the unit cell content of H₃P₈O₈N₉, but, in contrast, does not involve an interrupted network. This motif is characterized by 8-ring layers interconnected by additional pairs of tetrahedra. In P74O59N84 and $P_{40}O_{31}N_{46}$, these patterns are interconnected by additional building blocks. These build up arrays of layers perpendicular to two crystallographic directions. These intersecting layers form channels along [010], in which the H₂P₈O₈N₉like motifs are embedded. The additional layers mainly contain vierer rings. In P40O31N46, one type of these additional layers is thicker and less corrugated than in P74O59N84. Taken as a whole, all structures are mainly built up from dreier, vierer, sechser and achter rings.

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Keywords: microfocus diffraction, phosphorus nitride oxide, tertrahedra networks

Crystallographic characteristics of the siliceous lithic material from the deposit and the outcrops to explore the supply sources of Mesolithic groups from the Los Canes cave

María de Uribe-Zorita1, Celia Marcos1

1. Departamento de Geología; Universidad de Oviedo, Oviedo, Spain

email: mariatiska96@gmail.com

The crystallographic and mineralogical characterization (macroscopic and microscopic) of the Mesolithic lithic raw materials allows to analyze the establishment of mobility and exchange patterns; identify the adequacy between the technical processes of manufacturing and the selected raw material and find out the development of strategies in the acquisition and selection of lithic resources.

Only a few attempts have been undertaken to use the crystallinity of flint or the moganite content of chert for alternative or additional characterization and discrimination of lithic material (Bustillo et al., 2009; Graetsch and Grünberg, 2009).

In order to relate the lithic materials of the Los Canes cave (eastern Asturias, Spain) with possible supply outcrops a crystallographic study has been made with X-ray powder diffraction in order to identify and quantify the crystalline phases and obtain crystallographic data (crystal size, lattice strain, etc.) of them for comparision. Analyses with the scanning electron microscope + EDX and Infrared spectra were also considered.

Los Canes cave, with indications of Mesolithic human activity, in the interior part of the Asturian region on the northeast edge of the Hesperian chain that constitutes the substratum of the Iberian Peninsula. This region is mainly constituted by Palaeozoic rocks (with ages ranging from the Middle Cambrian to the Upper Carboniferous (Alonso and Pulgar, 1995) elevated by the Alpine orogeny, which created a typical Germanic geomorphology. Flint does not occur very frequently in this region, but some of them, of Lower Carboniferous age, can be found in the Picos de Europa region. The tectonic movements related to the Variscan orogeny displaced and eroded these materials towards the south. The Alpine orogeny of the Tertiary era and the Quaternary glacial and fluvial erosion configured the current relief, relocating part of the flints (Marquínez and Adrados, 2000). Additionally, at both edges of the region some accumulations of flint can be found in some small remains of Mesozoic basins.

The Mesolithic main materials knapped in the Los Canes cave were grey flint, black flint, radiolarite, Pendueles chert, Cretaceous flint, quartzite and quartz; quartzite is the dominant raw material in weight, except in the Late Mesolithic phase of the site, dated to the sixth millennium cal BC, where this raw material drops sharply and flint reaches 63.3% (Arias et al., 2009). These varieties were recognized in the field, in different outcrops.

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Keywords: Flint, Los Canes, Mesolithic

Theoretical polytypism and practical twinning of aragonite crystals

Pavel Gavryushkin1, Alexander Re'cnik2, Nina Daneu2

- Novosibirsk State University, Laboratory of experimental geochemistry and petrology of the Earth's mantle; Sobolev Institute of Geology and Mineralogy, Laboratory of theoretical and experimental study of high-pressure minerals, Novosibirsk, Russia
- 2. Department for Nanostructured Materials, Jo*zef Stefan Institute, Ljubljana, Slovenia

email: p.gavryushkin@gmail.com

In the present work, we show the results of investigation of aragonite (CaCO₃) microstructure with transmission electron microscopy (TEM) under ambient and elevated temperature, complemented by density functional theory calculations. As objects of investigation we choose crystals from Tazouta (Marocco), Cuenca (Spain), and Koge-Dava (Russia) localities. All crystals were well faceted, 1-3 centimetres length. Different localities were chosen to cover different genesis, morphology and chemistry.

The ubiquitous twinning by $\{110\}$ down to unit cell size was found on all studied crystals. In some areas twinning is so dense, that these areas can be considered as disordered polytype of aragonite. The super-structural reflections (0.5 0.5 0) were found on [1-10] projection. We suggest that these reflections arise from the diffraction on numerous twinning planes, locally doubling d(110). Also strong reflections prohibited for aragonite symmetry was found in [1-10] projection. Appearance of prohibited reflections can be explained by the presence of flattened domains with decreased symmetry.

Calculated enthalpies of polytypes, produced by ordered twinning by {110}, shows that at 0 K enthalpies of O4-O16 polytypes are even lower than the enthalpy of aragonite. This is consistent with ubiquitous twinning by {110} in both organic and inorganic samples and characterise this twinning as the fundamental feature of aragonite structure. Calculated Gibbs energies indicate that temperature energetically stabilise aragonite relative to other polytypes, which explains absence of ordered polytypes in real crystals.

On heating of powder sample above 350C, satellites reflections appear in [1-10] zone axis. One of the possible explanations of such changes is the generation and ordering of {110} twin boundaries. It was theoretically shown [1] that mechanical twinning taking place during aragonite grinding [2] is realised by the shift of {110} layers of aragonite structure. In our work, we suggest another mechanism of {110} twin boundaries generation, more appropriate for high-temperature conditions.

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Keywords: microstruture, twinning, TEM

MS13-P10

Solid-state synthesis and structural characterization of novel geo-inspired sulfate, Na₂CuM₂(SO₄)₄ (*M*=Mg, Zn)

Oleg Siidra¹, Diana Nekrasova¹-²; Zhuici Chen¹, Vadim Kovrugin¹-², Olivier Mentre², Marie Colmont²

- Department of Crystallography, St. Petersburg State University, 199034 St. Petersburg, Russia, Saint-Petersburg, Russia
- Unité de Catalyse et Chimie du Solide (UCCS), UMR 8181, Université Lille 1, 59655 Villeneuve d'ASCQ, France

email: siidra@mail.ru

Sulfates attract considerable attention due to their wide distribution in nature. A large group of anhydrous sulfate minerals is formed in high-temperature exhalative processes in fumaroles of volcanoes. Many of the exhalative minerals demonstrate unique structure types and may be of interest from the view point of materials science.

Itelmenite, Na₂CuMg₂(SO₄)₄, was recently found in a fumarole of the Naboko scoria cone of the Fissure Tolbachik volcano eruption (2012-2013), Kamchatka Peninsula, Russia [1]. [M^{2+}_{3} (SO₄)₄]² sulphate framework in itelmenite is unique and has not been described before in minerals or synthetic compounds. Sulphate tetrahedra are packed into pseudolayered arrangements perpendicular to the *a* axis. Structure topology of itelmenite is rather simple. Each MO_5 or MO_6 polyhedron shares all common corners with sulphate tetrahedra thus forming heteropolyhedral framework with voids filled by Na⁺ cations.

Single crystals of Mg- and Zn-dominant synthetic analogues of itelmenite were grown by the solid-state reaction from the mixture containing equimolar quantities of anhydrous CuSO₄, Na₂SO₄, MgSO₄ or ZnSO₄. Na₂CuMg₂(SO₄)₄ (1) and Na₂CuZn₅(SO₄)₄ (2) are orthorhombic, *Pbca*. 1: *a* = 9.531(6) Å, *b* = 8.745(6) Å, *c* = 28.72(2) Å, *V* = 2393.3(3) Å³. **2**: *a* = 9.458(5) Å, *b* = 8.811(4) Å, *c* = 28.850(15) Å, *V* = 2404(2) Å³. Mixed cationic character of *M*1, *M*2 and *M*3 sites is similar to that observed in natural sample. Symmetrical *M*3 octahedral site is occupied exclusively by Mg and Zn in the structures of **1** and **2**, respectively.

Obtained materials were investigated using powder X-ray diffraction, high-temperature powder X-ray diffraction, IR spectroscopy and DSC-TGA.

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Keywords: sulphates, minerals, materials

In-situ temperature X-Ray diffraction and mechanical study of the binary yellow 18-carat gold alloy AuCu

Mohammed Said M. Abdelbaky¹, Imene Lamiri², David Martínez Blanco³, Djamel Hamana², Santiago García Granda¹

- Department of Physical and Analytical Chemistry, University of Oviedo-CINN, Oviedo, Spain
- Research Unit of Material Science and Applications, Science Faculty, University Constantine 1, Constantine, 2500- Algeria, Constantine, Algeria
- Scientific and Technical Services, University of Oviedo-CINN, Oviedo, Spain

email: saidmohammed.uo@uniovi.es

Regarding to the huge impact that have the phase transition sequences and temperatures on the physical properties of the alloys, the study of these phenomena has a practical importance[1-3].Herein, In-situ temperature XRD and mechanical spectroscopy were applied to study phase transitions in AuCu alloy. The measurements have been carried out from room temperature up to 973K from the ordered state AuCuI as starting phase. The phase transition sequences, was investigated upon heating using heating rate of 1K/ min. The sequences of phase transitions presentimportant results that depend crucially to the starting state. This transition sequences determine temperature dependency of elastic and anelastic properties. The mechanical spectroscopy using forced torsion pendulum shows twin boundaries peak as typical peak of the orthorhombic phase AuCuII according to the thermal tests. The isothermal frequencies measurements have shown the behaviors of the thermally activated peaks in the phase transitions intervals.

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Keywords: Gold alloys, in-situ temperature XRD, mechanical spectroscopy

MS13-P12

High-Accuracy measurement of cell dimensions of the vanadium α- and β-phases in V-O System

Boris Kodess¹, Igor Kommel¹, Vladimir Volodin¹, Alexander Alpatov², Sergey Muradyan²

1. CMD, Materials Science -VNIIMS-ICS&E, Moscow, Aurora, Russia 2. IMET RAS, Moscow, Russia

email: kodess@mail.ru

We observe traceability of high-purity vanadium properties in the oxides and chemical bonds of minerals and related materials. High-accuracy measurements using conventional and synchrotron X-Ray methods have been carried out to determine structural characteristics of single crystals zone melting vanadium. The impurity content for possible 34 elements in the investigated crystalline samples was estimated, using an M1 Mistral micro-fluorescence spectrometer (of Bruker firm). The vanadium content was estimated from the measurement results as 99.98%. The oxygen and nitrogen content (mass fraction, %) in the samples was determined using a TC600 analyzer (LECO), by reducive melting in a graphite crucible in an inert gas (helium) flow. The hydrogen content was determined using the RHEN602 analyzer (of LECO firm) by reducive melting in a graphite crucible in an inert gas (argon) flow. The average value of oxygen concentration was 900 ppm w, nitrogen - 200 ppm w, and, importantly, hydrogen was only 40 ppm w. To assess the effect of the purity of single crystals on mechanical properties, Vickers hardness measurements (Hardness tester 930N from Wolpert firm) were performed. The obtained hardness value of 135 HV indicates the acceptable purity of the single crystals used.

Both types of samples - a-phase and \beta-phase - were investigated using a CCD detectors, MoKa1-radiation, and a wavelength of 0.070932 nm. 1900 to 2500 Bragg reflections were collected for each of the three samples for the a-phase at room temperature, to fill to maximum the entire Ewald sphere. The spatial group of the unit cell is Im-3m (No. 229). The average value of the three experiments of the unit cell dimension (lattice constant) was 0.303465(5) nm. Two similar complete experiments were performed in the same way for spherical single crystals of the vanadium β-phase. At room temperature, from 2200 to 2800, the Bragg reflections are collected. It was found that the value of one of the dimensions of the unit cell of the β -phase was a = 0.30409(2), which was close to the value of the lattice constant of a-phase of vanadium. For the second constant of the tetragonal unit cell, the value was b = 0.3373(5) nm. The latter value noticeably increased because of additional introduction of oxygen into this unit cell. Thus, the use of data on the original elements with a minimum content of oxygen impurities allows to extract and establish the inherited structural features in various vanadium-content chemical compounds and alloys [1-3]

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Keywords: vanadium-oxygen system, unit cell dimension, inherited structural features

High-Accurate Measurement of Cell Dimensions of Niobium α-phase in Niobium-Oxygen System

Maksim Reylyanu¹, Boris Kodess¹, Igor Komme¹, Aleksandr Alpatov²

- 1. VNIIMS, Moscow, Russia
- 2. IMET RAS, Moscow, Russia

email: makc.200606@gmail.com

We observe traceability of high-purity niobium properties in the oxides and chemical bonds of niobium-content chemical compounds minerals and related materials [1-3]. Two approaches for the determining of the structural characteristics of niobium are used. The first variant compares our and different results of X-ray studies of "oxygen-free" niobium using conventional and synchrotron X-Ray methods. After additional annealing of samples in ultra-high vacuum and at high temperatures, the oxygen content in the samples does not exceed 0.03 % mass. The nitrogen concentration is very small 9±1 ppm w, the average content oxygen in these samples is 0.015 \pm 0.003% (mass fraction).

The second variant of approach use extrapolates dependence of the unit cell dimension from the oxygen content obtained for samples of the Nb-O system. The impurity content has been estimated by X-ray fluorescence spectrometry on an M1 Mistral analyzer (of Bruker firm). The niobium content is estimated from the measurement results as 99.99% for possible 34 elements. A sample of the alpha-phase of niobium with an oxygen content of about 0.3 wt. % is investigated by single crystal X-ray diffraction. Two complete experiments were performed in the for spherical single, using a detector CCDs, MoKal-radiation and a wavelength of 0.070932 nm. At room temperature, from 2200 to 2800, the Bragg reflections are collected for the samples in order to fill to maximum the entire Ewald sphere. The spatial group of the unit cell is Im3m (No. 229). The average value of the two experiments of the unit cell dimension (lattice constant) is 0.33062(5) nm. This value is in good agreement with the results of six experiments given in the ICCD PDF-database.

Based on the results of the experiments of the increased accuracy and data from the references, the dependence of the value of the unit cell dimension of niobium on the oxygen content has been plotted. Linear extrapolation to zero value results in a value of a=0.32988(5) nm. This value is in good agreement with the data on unit cell dimension for "oxygen-free" niobium a=0.33005(2) nm. Thus, this dependence can also be used to estimate the oxygen content in various samples of the alpha-phase in the Nb-O system. Such samples with low content of oxygen are used also to create more efficient thermal converters. Thin protective layers of coatings of niobium oxides are also widely used in various spheres of the industry.

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Keywords: high-purity Niobium, system Nb-O, unit cell dimension

MS13-P14

Structural studies of crystalline phases occurring when temperature cycling a stabilised system of sodium sulfate decahydrate

Emily Goddard¹, David Oliver², Colin Pulham¹

- 1. EaStChem School of Chemistry, University of Edinburgh, Edinburgh, United Kingdom
- 2. Sunamp, Macmerry, United Kingdom

email: s1112015@sms.ed.ac.uk

Salt hydrates represent a class of compound with a high latent heat of energy; they absorb a large amount of heat upon melting and release it upon re-crystallisation. They form part of a group of materials known as phase-change materials (PCMs), which are of great interest in the field of heat storage. Each PCM has a defined melting point and energy density and can therefore be tailored for different applications. The materials should show a stable performance over thousands of charge-store-discharge cycles, with no degradation in performance. They should also nucleate reliably and crystallise at a suitable rate. However, few systems fit this profile.

Sodium sulfate decahydrate (Na₂SO₄.10H₂O) is a good candidate for storing low-grade solar energy. However, it melts incongruently, decomposing into a mixture of the anhydrous Na₂SO₄ and a solution of salt in water. Upon formation, the dense anhydrous salt precipitates out to the bottom of the container, decreasing the concentration of the active PCM in the system, so the amount of heat stored decreases with each cycle. Various approaches have been trialled to supress the incongruent melting and allow the system to be used as a PCM.

This poster describes the development of a method that supresses the formation of the anhydrous salt, allowing the system to be cycled reliably, reversibly and reproducibly. Crystallographic techniques were used to identify and characterise the various crystalline phases that appeared during temperature cycling of the system.

Keywords: heat storage, phase-change materials, incongruent melting

Structural characteristics of vermiculites treated with alcohol

Zulema del Rio Rivadulla¹, Celia Marcos Pascual¹

1. Department of Geology, University of Oviedo (Asturias, Spain)

email: zulema1699@hotmail.es

As a result of its lamellar structure, vermiculite exhibits various properties related to structural features, such as the sheet loading associated with the numerous isomorphic substitutions or the ability to dehydrate and rehydrate. It is an interesting mineral in physics, chemistry and biology and very attractive due to its numerous thermal applications and as an insulator. In addition to water, vermiculite can adsorb inorganic or organic substances in the expandable interlayer. Among the various studies conducted on the intercalation of polar organic molecules by clay minerals, the most studied are those related to the adsorption properties of alcohols (Bergaya et al., 2006).

Two vermiculites from China and Libby were treated with different alcohols (methanol, ethanol, propanol and butanol), at room temperature, for 1 month, and subsequent microwave irradiation, for 20 seconds. This treatment caused structural changes and expansion of the vermiculites. The structural changes were characterized by x-ray diffraction, infrared spectroscopy and scanning electron microscopy. The results indicated: 1) The appearance of extra interstratified phases during the transformation from 2- to 1-WLHS (Water Layer Hydration States); 2) the improvement of the crystallinity and order of the most phases, which are the same phases of the untreated vermiculites or even some more. The expansion, k, was measured by the change of the apparent density (k=density of the raw sample/density of the treated sample) (Justo et al., 1989). Expansion is related to the water loss, composition and distribution of vermiculite cations. Thus, the Fe2+ ions would facilitate the fixation of the K+ ions but not the water, so that the amount would be lower (Marcos and Rodríguez, 2010). The expansion with microwaves irradiation of the samples treated with alcohol varied related to starting sample and time of alcohol treatment. It was also observed that some particles expanded and others did not, as reported previously by Marcos and Rodríguez (2011). The objective of this work was to relate the expansion to structural changes induced in the investigated samples and to the potassium migration.

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Keywords: vermiculite, alcohol, exfoliation

MS13-P16

Piezoelectric phase transition in KSrVO4 investigated using the Aeris diffractometer

Jan Gertenbach1, Gwilherm Nénert1

1. Malvern Panalytical, Almelo, Netherlands (Holland, Europe)

email: jan.gertenbach@panalytical.com

The rich crystal chemistry of A¹B¹¹XO₄ (A¹ = alkali ion, B¹¹ = alkali-earth ion, X = P, V, As) leads to numerous polymorphic phases that have related structural families, such as olivine (e.g. LiMnPO₄), arcanite (β-K₂SO₄), glaserite, tridymite, α -K₂SO₄, β-Na₂SO₄ and γ -Na₂SO₄ [1]. Among the various families (X = P, V, As), the phosphates have been most widely studied. In addition to their interesting crystal chemistry behaviour, research on this family of materials is mainly driven by their ferroelectric-, and ferroelastic properties as well as possible applications as phosphors for LEDs [1].

In recent years, we have investigated several structural combinations of the A'B^{II}VO₄ type [2] and a new crystal type within this family was identified, namely a form of NaSrVO₄ that is isostructural to larnite [2]. In this work, we continue our exploration of the A'B^{II}VO₄ family by investigating the composition of KSrVO₄. While NaSrVO₄ crystallizes in the P2₁/n space group, divergent results are reported for KSrVO₄. Single crystal work suggests Pnma symmetry [3], but powder diffraction studies show evidence for P2₁2₁2₁ symmetry with distinct reflections present that are not consistent with Pnma symmetry[3]. These contradicor of the compound as a function of temperature.

Using the Aeris benchtop diffractometer equipped with the BTS 500 non-ambient chamber, the crystal structure of KSrVO₄ was studied in the 25-500°C range. At room temperature the structure is best described as having P2₁2₁, symmetry, allowing for piezoelectricity in this material. By increasing the temperature, it is possible to observe a phase transition to Pnma symmetry. This phase transition appears to be related to the piezoelectric nature of the material and its associated spontaneous strain.

This work reports on the first purely gyrotropic phase transitions in the $A^{1}B^{11}VO_{4}$ family.



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Keywords: phase transitions, spontaneous strain, benchtop XRD

MS14- Combined approaches for structure characterization of modulated and complex structures

Chairs: Prof. Joke Hadermann, Dr. Phillipe Boullay

MS14-P01

Structure elucidation of a zeolite with multi-dimensional disorder by combining HRTEM and XRPD analyses

Magdalena O. Cichocka¹, Yannick Lorgouilloux², Stef Smeets¹, Philippe Caullet³, Nicolas Bats⁴, Lynne B. McCusker⁵, Jean-Louis Paillaud³, Xiaodong Zou¹

- 1. Department of Materials and Environmental Chemistry, Stockholm University, Stockholm , Sweden
- Univ. Valenciennes, EA 2443 LMCPA Laboratoire des Matériaux Céramiques et Procédés Associés, Valenciennes, France
- Université de Haute-Alsace, CNRS, Axe Matériaux à Porosité Contrôlée (MPC), IS2M UMR 7361, Mulhouse, France
- 4. IFP Energies nouvelles, Rond Point de l'échangeur de Solaize -BP 3, Solaize, France
- 5. Department of Materials, ETH , Zurich, Switzerland

email: magdalena.cichocka@mmk.su.se

We present a detailed structure analysis of zeolite IM-18 with a complex disordered framework structure that was unknown for more than 10 years.^[1,2]IM-18 has a novel framework topology and a three-dimensional 8x8x10-ring channel system, making it ideal for the shape selective catalysis of small molecules. The unique disorder in the structure makes the structure analysis complicated, so we combined three complementary techniques, including single-crystal electron diffraction (SCED), high resolution transmission electron microscopy (HRTEM) and synchrotron X-ray powder diffraction (XRPD) to reveal the details of the disorder.

Solving the structure of a polycrystalline material that is also disordered can be very challenging as there are no standard procedures to follow. Rotation electron diffraction (RED) allowed us to solve the average structure of the material, the local ordering was observed from the HRTEM images (Fig. 1B-E), but the fine details of the structure and location of the OSDA and Ge could only be derived from XRPD data (Fig. 1A). We found that IM-18 contains two different types of stacking faults along two directions, which were difficult to observe using HRTEM because of the beam sensitivity of the material. We could describe the structure as 1D longrange ordered and 2D disordered, which culminates in a mixture of four types of domains.

By using such an approach, we not only demonstrated the general procedures for *ab initio* structure elucidation of disordered nanocrystals, but also the potential that the combination of SCED, HRTEM and XRPD offers.



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Keywords: combined methods, disorder, zeolite

MS14-P02

NMR crystallography of beryl minerals at 9.4 T and 19.6 T

Luis Sánchez Muñoz¹, Isabel Sobrados², Jesús Sanz², Virginia Diez², José Ignacio Santos³, Javier García-Guinea⁴, Federico Pezzotta⁶, Sandra Brito Barreto⁶, Zhehong Gan⁷

- 1, Instituto de Cerámica y Vidrio (CSIC), Madrid, Spain
- 2. Instituto Ciencia de Materiales de Madrid (CSIC), Madrid, Spain
- 3. SGIker-UPV/EHU, San Sebastián, Spain
- 4. Museo Nacional de Ciencias Naturales (CSIC), Madrid, Spain
- 5. Museo di Storia Naturale, Milano, Italy
- 6. Centro de Tecnologia e Geociências Universidade Federal de Pernambuco, UFP, Pernanbuco, Brazil
- National High Magnetic Field Laboratory, FLU, Tallahassee, United States of America

email: lsm@icv.csic.es

The available description of the aluminosilicate beryl group of minerals suggests RX₃Al₂(Si₆O₁₈)·H₂O as general formula, with beryl Be3Al2Si6O18 (P6/mcc) and pezzottaite Cs(Be-2Li)Al2Si6O18 (R-3c or R3c) as end-members. It involves a wide diversity of intermediate chemical compositions because the structure can incorporate different alkali atoms in solid solution, located at channel R site and tetrahedral X sites, and H2O molecules in the structural channel. Reciprocal-space techniques have resolved only average structures in the intermediate members, related to one of the two the ideal crystal structure of the end-members, and have difficulties in the study of water molecules. Here, high-resolution multinuclear NMR spectroscopy, leading to ²⁹Si, ²⁷Al, ⁹Be, ¹³³Cs, ⁷Li, ²³Na and ¹H spectra at 9.4 T as well as ²⁷Al and 9Be spectra at 19.6 T, has been used to investigate the short- and medium-range structures in nine specimens along the solid solution of this group. The 1H NMR SP and CP experiments suggest that hydrogen atoms are actually as OH groups for compensation of local charge, instead of water molecules which were detected in very low concentration. The structural description by reciprocal-space techniques and NMR coincides only in the alkali-free perfectly longrange ordered P6/mcc beryl end-member, which in fact is extremely rare in Nature, having one tetrahedral site for Si atoms, one octahedral site for Al atoms, and one tetrahedral site for Be atoms. However a tectosilicate description seems more appropriated that a cyclosilicate classification from the values of the 29Si chemical shifts, as Be and Si atoms form a Q4 configuration. The most common mineral is alkali-rich beryl having a crystal structure with lower local symmetry than the ideal average hexagonal structure, with at least two sites for Si atoms, four sites for Be atoms, two R sites and two X sites for Li atoms, two R sites for Na atoms, one R site Cs atoms, and two types of OH groups. The NMR data of pezzottaite indicate six tetrahedral sites for Si atoms, two octahedral sites for Al atoms, one tetrahedral site for Be atoms, two R sites and two X sites for Li atoms, three R sites for Cs atoms, and two types of OH groups with one of them different from that of beryl. The lack of resolving power of diffraction techniques to resolve the structural detail of non stoichiometric beryl is similar to that found in order-disorder series of K-feldspars (Sánchez-Muñoz et al. 2013).

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Sánchez-Muñoz, L.; Sanz, J.; Sobrados, I. & Gan Z.H. (2013) Am. Mineral., 98, 2115-2131

Keywords: NMR crystallography, local structure, beryl

MS14-P03

Application of the full-symmetry Patterson sum-function to the solution of complex cluster-based minerals from powder diffraction data

Jordi rius1

 Institut de Ciència de Materials de Barcelona (CSIC), 08193 Bellaterra, Catalonia, Spain

email: jordi.rius@icmab.es

Often, poorly growing minerals are based on self-assembly of metal clusters e.g. via H bond networks [1]. If the unit cell and the space group symmetry of these compounds can be estimated from the powder diffraction pattern, then this information can be used 1) to extract the cluster intensities from the pattern 2) to strengthen the Patterson sum-function application (S_P) [2] by reducing the number of phases to be refined (the S_P -FT algorithm is implemented in the XLENS PD6 code retrievable from https://departments. icmab.es/crystallography/software). Unlike direct-space structure solution methods, the Sp -FT algorithm is especially well-suited for crystal structures containing cations with irregular or unpredictable coordination polyhedra or when some structural disorder is present. Although this algorithm was initially developed for organic compounds, it will be shown that it is also suitable for the location of light atoms in the presence of a large number of heavy atoms.

In those cases where the unit cell cannot be found directly from the powder pattern, electron diffraction tomography (EDT) constitutes an alternative way of solving the crystal structure.. However, its efficiency decreases if the sample is sensitive to vacuum induced dehydration. It will be shown that even in such unfavorable circumstances the information provided by EDT is complementary to that of PD and can be used to advantage by the S_p -FT algorithm. This will be illustrated on the solution of the unknown crystal structure of decrespignyite-(Y), a new complex copper yttrium rare-earth carbonate chloride hydrate from Paratoo (South Australia) [3].

The public financial support through project MAT2015-67953-P of MINECO/FEDER is gratefully acknowledged.

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Keywords: full-symmetry Patterson sum function, ab-initio structure solution, powder diffraction

MS14-P04

Atomic displacements in yttriummanganese-oxide with and without fesubstitution, revealed by resonant X-ray diffraction

Melanie Nentwich¹, Carsten Richter², Tina Weigel¹, Matthias Zschornak¹, Dirk Meyer¹

- 1. Experimental Physics, TU Bergakademie Freiberg, Freiberg, Germany
- 2. ID01, ESRF, Grenoble, France

email: Melanie.Nentwich@physik.tu-freiberg.de

Yttrium-Manganese-Oxide YMn2O5 (YMO) is studied since 1973 due to its remarkable magnetic properties, e. g. different modulation phenomena and several respective phase transitions. The ambient temperature phase of YMO is paraelectric and paramagnetic. The lattice has the orthorhombic space group Pbam (55) and its building units are [MnO₅] pyramides and [MnO₆] octahedra, the latter forming chains along the c direction. At 45 K, 40 K, 39 K and 19 K, the structure changes between several magnetic modulations [1]. Here, we are interested in the commensurate modulated phase between 39 K and 19 K. Presumably within space group $Pb2_1m$ (26), the respective lattice modulation vector is 0 0 $\frac{1}{2}$, whereas the polarization points along b. However, crystal structure refinements in a non-centrosymmetric space group showing polar displacements have not yet been successful. Moreover, there is still disagreement about the interplay of magnetic superstructure and a polar displacement pattern. To analyze possible displacements of the commensurate phase in detail, we apply the newly developed and highly sensitive Resonant X-ray Diffraction (RXD) Method REXSuppress that uses destructive interference of the intensity at carefully chosen Bragg reflections [2]. For this structure analysis, we determined atomic displacement parameters (ADP) of the high and low temperature phase with the same method and surveyed the appearance of superstructure reflections that would accompany the transition to space group $Pb2_1m$ (26).

Additionally, we examined the distribution of Fe in Yttrium-Manganese-Iron-Oxide (YMnFeQ₂), which results from the substitution of 50% Mn. The element- and site-selectivity of RXD is capable of separating the two distinct Mn Wyckoff sites (pyramide and octahedron), in particular with the octahedral site possessing forbidden reflections (reflection condition hkl with h + k = 2n). Thus, the question of occupation is easily accessible and will be treated similar as by [3].

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Keywords: refinement, mullite, commensurate

MS15- Crystallography in Earth and space

Chairs: Dr. Anna Pakhomova, Prof. JuanMa García-Ruiz

MS15-P01

Evidence of screw dislocation on gypsum crystals as principal mechanism of growth at low supersaturation

Joaquin Criado Reyes¹, Linda Pastero², Marco Bruno², Dino Aquilano², Fermín Otálora Muñoz¹, Juan Manuel García Ruiz¹

- 1. Laboratorio de Estudios Cristalográficos, IACT UGR-CSIC, Granada, Spain
- Dipartimento di Scienze della Terra, Università degli Studi di Torino, Torino, Italy

email: joaquin.criado@csic.es

Gypsum mineral mainly occurs on evaporitic environment around the world [1, 2]. It has also been reported as a relevant phase in Mars [3-5]. The growth conditions during the growth of gypsum crystals influences the surface growth mechanisms and the habit. Many authors suggest that the growth mechanisms of gypsum crystals at low supersaturation is due to dislocation growth, these studies are based on kinetic data fitted to theoretical equations[6, 7]. However, the observation of hillocks on the surface gypsum crystals has been challenging. A couple of studies on the cleavage face (010) of gypsum by Atomic Force Microscopy (AFM) and Differential Interface Contrast Microscopy (DICM) shown some hillock but only one of them could be clearly identified as a screw dislocation, so the authors conclude that the main growth mechanism at low supersturation on this face is by 2D nucleation[8, 9]. Equivalent studies on the (120) face are missing, mainly due to the roughness of these faces. In a preliminary study of the gypsum (120) face using crystals growing by evaporation, we observed that hillocks spread on (120) at low supersaturation. Those hillocks are made by monolayers with a height of 4.30 Å corresponding to the d-spacing. These hillocks show an asymmetric morphology (figure 1).



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Keywords: Gypsum, Growth Mechanism, Screw Dislocation

MS15-P02

Synthesis and crystallographic study of laflammeite (Pd₃Pb₂S₂) and thalhammerite (Pd₉Ag₂Bi₂S₄)

Frantisek Laufek¹, Anna Vymazalová¹, Sergei F. Sluzhenikin², Vladimir V. Kozlov³, Jakub Plášil⁴

- 1. Czech Geological Survey, Prague, Czech Republic
- Institute of Geology of Ore Deposits, Mineralogy, Petrography and Geochemistry RAS, Moscow, Russia
- 3. Oxford Instruments (Moscow Office), Moscow, Russia
- 4. Institute of Physics ASCR, Prague, Czech Republic

email: frantisek.laufek@geology.cz

Mineral laflammeite (Pd₃Pb₂S₂) was firstly described by Barkov et al. (2002) from the Kirakkajuppura platinum-deposit, Penikat layered complex, Finland. Barkov et al. (2002) provided chemical and physical characterisation of this mineral, however its detailed crystal structural analysis has been lacking. Thalhammerite (Pd₉Ag₂Bi₂S₄) was discovered in millerite-pyrite-chalcopyrite vein-disseminated ore from the Komsomolsky mine in the Talnakh deposit, Russia (Sluzhenikin and Mokhov, 2015). Crystal structures of both minerals and relevant crystal-chemical implications will be presented.

Laflammeite occurs as subhedral platelets up to 150 μ m, however the crystals are finely twinned and consequently unsuitable for a direct crystal structure study (Barkov et al. 2002). Thalhammerite occurs as tiny inclusions (from few μ m up to about 40-50 μ m) in sulphide ore where it forms intergrowns with other Pd-bearing minerals. Therefore, both minerals were synthetized by silica glass tube technique by heating at 400 °C from stoichiometric mixture of elements. The prepared synthetic analogues of laflammeite and thalhammerite were used for a crystal structure study. The structural identity between natural and synthetic materials was subsequently confirmed by an electron-backscattered diffraction.

Laflammeite, Pd₃Pb₂S₂, crystalizes in *Pmmn* space group (a = 5.78, b = 8.18, c = 5.96 Å) and Z = 2. Its crystal structure show many similarities with structures of shandite (Ni₃Pb₂S₂, *R*3*m*), parkerite (Ni₃Bi₂S₂, *C*2*m*) and vymazálovaite (Pd-₃Bi₃S₂, *T*213). All these minerals show a common structure motive: a pseudocubic subcell of the CsCl-type composed of Bi(Pb) and S atoms. A half of available octahedral voids is occupied by Ni(Pd) atoms. The distribution of Ni(Pd) atoms (i.e. the ordering scheme) determines the structure type (Weihrich et al. 2007). Laflammeite can be considered as antiperovskites superstructures.

Thalhammerite, $Pd_9Ag_2Bi_2S_4$ shows I4/mmm symmetry (a = 8.02, c = 9.15 Å) and Z = 2. Its unique crystal structure is based on a three-dimensional framework which consists of two types of blocks of polyhedra that interpenetrate and support each other. The first type consists of corner-sharing [PdS₄] and [PdBi_2S_2] squares. The second is formed by flattened tetrahedra [PdBi_2S_2]. Silver atoms occupy channels running along the *c* direction. Thalhammerite crystal structure merges metallic building blocks with structure motives typical for polar sulphides.

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Keywords: crystal structure, new minerals, sulphides

MS15-P03

Carbon molecules in space: a thermal equation of state study of solid hexamethylentetramine

Giulia Novelli¹, Helen Maynard-Casely², Konstantin Kamenev¹, William G. Marshall³, Garry McIntyre², Simon Parsons¹

- 1. School of Chemistry and Centre for Science at Extreme
- Conditions, University of Edinburgh, Edinburgh, United Kingdom 2. Australian Nuclear Science and Technology Organisation, Sydney, Australia
- 3. ISIS Neutron and Muon Facility, Oxford, United Kingdom

email: s1794786@ed.ac.uk

Equations of State (EoSs) show how the thermodynamic variables of temperature (T), pressure (P) and volume (V) are inter-related. The ideal gas law, PV = nRT, is an example of an EoS which is used as a simple but effective model to explain the properties of gases. EoSs can also be applied to solids, where they can be used to show how energy changes when the solid experiences dramatic changes in its environment. Such information is relevant to understand the fate of carbon in the context of planetary settings, from comets to gas giants. Despite the large heterogeneity of galactic and interstellar regions, the organic chemistry of the universe seems to follow common pathways. Molecules of high astrobiological relevance such as N-heterocycles and amino acids have been identified in trace quantities in meteorites but they can be considered fragile species easily destroyed by raditions, shocks and thermal processes through the Solar System.

Alhough it is quite common to model thermal expansion at ambient pressure with a VT equation of state (EoS), and compression using a PV EoS, determinations of PVT EoSs are much less common, particularly for molecular materials. The paucity of data reflects the difficulty in varying pressure and temperature simultaneously in crystallographic experiments, especially at reduces temperatures. These difficulties are addressed by the variable temperature insert for the Paris-Edinburgh cell available on the PEARL instrument at the ISIS Neutron Spallation Source.

A PVT EoS provides access to a rich array of thermodynamic properties which revel the changes in different contributions to the thermodynamic properties such as internal energy, enthalpy and entropy occur in response to compression. The same quantities can be modelled using computational methods such as the PIXEL method and Density Function Theory, making EoS measurements sensitive tests of theory. This poster will describe a PVT EoS determination for hexamethylentetramine- d_{12} a high-symmetry crytalline solid which remains in the same phase from 130 to 480 K and between ambient pressure and 5 GPa.

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MS15-P04

Evolution of uranyl-bearing structural complexes

Vladislav Gurzhiy¹, Sergey Krivovichev¹

1. St. Petersburg State University, Crystallography Dept., St. Petersburg, Russia

email: vladgeo17@mail.ru

Uranyl sulfates and selenates are the most remarkable groups of U6+-containing compounds due to their mineralogical importance and fascinating variety of structural topologies and topological isomers. The unique diversity of these materials can be explained by the high topological and structural adaptability of uranyl-based structural units to the charge and shape of organic and/or inorganic complexes that compensate for the negative charge of the uranyl complexes. Due to the small energetic differences between distinct topologies with the same overall composition, the structures of uranyl-based units may adapt to a particular template through topological and geometrical variations, thus demonstrating considerable structural flexibility. The interesting problem that appears in this regard is how complexity of a particular topological structure is related to the shape and complexity of templating ions.

Within the conceptual framework of the information-based approach, uranyl-containing 1D and 2D units have been investigated using topological approach and information-based complexity measures demonstrating that very complex structures may form as transitional architectures between phases with relatively small amounts of structural information [1], wherein the overall trend shows that complexities of structures formed on the latter stages of crystallization are higher than those for the phases growing on the primary stages [2]. In addition, it was found that complex topologies form more rare than their simplest counterparts, which is a response of the crystal structure to changes of chemical conditions within the system [3].

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Keywords: Uranyl, crystal structure, structural complexity

MS15-P05

Structural diversity of terrestrial phosphides related to Fe-Ni-P system

Maria Krzhizhanovskaya¹, Sergey Britvin¹, Michail Murashko¹, Yevgeny Vapnik², Andrey Zolotarev¹

- Department of Crystallography, Institute of Earth Sciences, Saint-Petersburg State University, St. Petersburg, Russia
- 2. Ben-Gurion University of the Negev , Beer-Sheva, Israel

email: krzhizhanovskaya@mail.ru

The recent findings of terrestrial phosphides related to Fe-Ni-P triangle (Table 1) substantially expand our knowledge on this important cosmochemical system. We herein provide comparative crystal chemical characteristics of terrestrial phosphides vs. their counterparts of space origin. Crystal structures of some of the listed minerals are studied by both single crystal and powder X-ray diffraction. Special attention has been paid to the distribution of iron and nickel in their structures. The possibility of X-ray diffraction approach, involving anomalous scattering of $CoK\alpha$ -radiation at the Fe-K edge, is discussed.

| Mineral | Formula | Structural type |
|-----------------|--------------------------------|--------------------------------|
| Negevite | NiP ₂ | Pyrite |
| Zuktamrurite | FeP ₂ | Marcasite |
| Murashkoite | FeP | FeP |
| Halamishite | Ni ₅ P ₄ | Ni ₅ P ₄ |
| Transjordanite | Ni ₂ P | Fe ₂ P |
| Barringerite | Fe ₂ P | Fe ₂ P |
| Allabogdanite | (Fe,Ni) ₂ P | Co ₂ Si |
| Nickelphosphide | (Ni,Fe) ₃ P | Ni ₃ P |
| Schreibersite | Fe ₃ P | Ni ₃ P |
| Melliniite | (Ni,Fe) ₄ P | Cr ₄ Si |

Table 1. Natural phosphides in the Fe-Ni-P system

* The names of new phosphide minerals are highlighted by italic.

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Keywords: phosphides, crystal structure, mineral

MS15-P06

Biomineral indicators of hydrological, geological and climatic processes in the Arctic

Liudmila Reykhard¹, Nataly Shulga¹, Yekaterina Novichkova¹, Nina Kozina¹, Olga Dara¹, Philipp Sapozhnikov¹, Vyacheslav Gordeev¹, Nikolay Belyaev¹, Andrey Boev¹

1. P.P.Shirshov Institute of Oceanology of the Russian Academy of Sciences, Moscow, Russia

email: mollusc@mail.ru

Research of the biominerals formed by the living organisms under extreme conditions of the Arctic are very important for understanding biostructure formation processes. During the period from 2004 to 2018 numerous samples in water column, ice and bottom sediments were studied in the Arctic region (White, Barents, Kara, Laptev seas) including the polar area (Fig.1a). It was found that a variety of the biominerals was formed by processes of biologically controlled (sea ice, water column and bottom sediments) and induced (bottom sediments) biomineralization.

We determined that in the ice cover of the central Arctic in April 2015 (coordinates: 89°35.27'N 20°24.13'E) opal frustules and skeletons of plankton and sea ice microalgae dominated among biomineral structures (Fig.1b). Their vertical distribution is associated with structural and textural characteristics and mineral-geochemical features of the ice cover. Upper layer of the water column of the central Arctic contained carbonate biogenic components such as coccoliths of *Emiliania huxleyi* (in April 2008; depth: 70 m; coordinates: 88°35.20'N 15°59.92'E) (Fig.1c) and foraminifera shells along with the opal biostructures of diatoms and radiolarians.

Bottom sediments of the Arctic seas contained bioinduced minerals. They formed aggregates such as ferromanganese micro- and macroconcretions with goethite, buzerite, bernessite, siderite; pyrite framboids [1] (Fig.1d); nest-shape clusters of vivianite crystals (Fig.1e); carbonate concretions with cement from different types of crystals of magnesian calcite and aragonite [2] (Fig.1f). It was discovered that formation of bioinduced biominerals in local zones of the bottom sediments required not only the increased concentrations of the elements like Fe, Mn, P, S etc., but also a high content of the organic matter. The results of isotope studies (\deltaC13) showed participation of methane-oxidizing bacteria in the formation of carbonate concretions in bottom sediments of the Laptev Sea. Authigenic carbonate formation in the Arctic shelf seas can act as a biogeochemical filter mechanism limiting methane emissions from bottom sediments to the water column and atmosphere [2].

The diversity of the founded biominerals in various natural environments reflects the influence of hydrological, sedimentation and diagenetic processes and can be used as indicators for paleoreconstructions of the Holocene history of the Arctic [3].

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Keywords: Biomineral, indicator, Arctic

MS15-P07

Investigating the primitive Earth through crystals

Fermin Otalora1, Juan Manuel García Ruiz1

1. Laboratorio de Estudios Cristalográficos. Instituto Andaluz de Ciencias de la Tierra. CSIC/UGr, Armilla, Granada, Spain

email: ferminotalora@gmail.com

Crystallography has a long history in providing knowledge and methods for applications in other disciplines. The identification of minerals using X-ray diffraction is one of the most important contributions of crystallography to Earth Sciences. But crystals deteriorate during during the long geological history, getting dissolved, replaced or deeply modified. After these process, diffraction information is restricted or Inexistent. This happen specially for crystals in very old samples, like the Archean rocks (3500 My) that we have investigated. In these cases, the real crystals disapeared long time ago and the morphology of the crystal casts provides the only crystallographic information on the original mineral phase and the environment of crystal growth. Here, we investigate crystal pseudomorphs and crystal casts found in a carbonate-chert facies from the 3.48 Ga old Dresser Formation (Pilbara Craton, Australia) that host some of the oldest remnants of life. Any information obtained from these casts on the atmosfere or the sea were crystals grew is telling us about the environment where life started. We have used a combination of X-ray microtomography, energy-dispersive X-ray spectroscopy, and crystallographic methods to reveal the original phases of these Archean pseudomorphs. We found with a high degree of confidence that the original crystals forming in Archean times were hollow aragonite.



Keywords: Aragonite, crystal morphology, X-ray tomography

MS15-P08

Crystal growth of lead bearing phases at acidic conditions

Ana Roza Llera¹, Amalia Jiménez¹, Ester Benito¹

1. Department of Geology. University of Oviedo., Oviedo, Spain

email: ana.roza@gmail.com

Dissolution - crystallization reactions can control the uptake of heavy metal such as lead, which is harmful to human health if inhaled or ingested. When Pb-bearing aqueous solution interacts with carbonates and sulfates, the formation of secondary phases at the interface mineral-water plays an important role on both the migration and accumulation of this pollutant in earth surface systems. The interaction of lead dissolved with calcium bearing minerals has been previously studied at pH between 4.75 and 6.8 [1-2]. However, less attention has been paid to the crystallization of Pb-bearing minerals in high acidic environments, in which the availability and mobility of dissolved Pb increase. Here, we have studied the interaction of Pb dissolved with both calcite and gypsum at highly acidic and atmospheric conditions. The main goals of this work were (a) to analyse the physicochemical evolution of the system and (b) to study the nature and morphology of the neo-formed phases. With these aims, a set of macroscopic experiments has been carried out by placing 1 g of crystals of a mix of calcite and gypsum (3.0 - 4.0 mm) in batch reactors containing 100 mL of Pb-bearing aqueous solution at pH= 2.5. Then, the vessels were closed with parafilm to minimize evaporation during reaction times (from 1 hour to 48 hours). The parent solution was prepared using reagent-grade Pb(NO₂)₂ and high-purity deionized water to yield [Pbaq]initial of 500 mg/L. After given period of time, the solid phases were analysed by glancing incident X-ray diffraction (GIXRD), Raman spectroscopy (RS) and Scanning Electron Microscopy (SEM). The initial and final pH were monitored and Ca²⁺ and Pb²⁺ in the aqueous solutions were analysed by ICP-OES.

Results show that dissolution of calcite and gypsum is simultaneous to elimination of the almost Pb^{2*} . Anglesite (PbSO₄) were identified using RS and GIRDX in all interaction experiments with gypsum. SEM reveals the heterogeneous nucleation of anglesite crystals, which are distributed randomly without covering all the gypsum surface. Different morphologies of anglesite are identified, including small rhombus-shaped single crystals, aggregates of identical crystals growing in parallel and contact twins. On the contrary, calcite is dissolving during the entire period of reaction and lead-bearing carbonates are not detected on the calcite surfaces. These data show that anglesite is a stable phase responsible of the Pb elimination under acidic conditions. The evolution of the anglesite morphologies after given reaction periods are discussed.

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Keywords: Lead, Calcite, Gypsum

MS16- Understanding of functional materials

Chairs: Dr. Oleg Siidra, Dr. Claire Colin

MS16-P01

$\begin{array}{l} Synthesis structure determination of béta-\\ K_{0.399}V_{2.623}W_{0.377}O_{7.5} \mbox{ with mixed occupation} \\ of vanadium and tungsten elements \end{array}$

Djillali Mezaoui¹, Sabrina Belkhiri², Olivier Perez³

- 1. U.S.T.H.B, Laboratoire des Sciences des Matériaux, Faculté de chimie, Alger, Algeria
- Université de Boumerdès, Laboratoire Sciences des Matériaux, L.S.M, Boumerdès, Algeria
- Laboratoire de cristallographie et Sciences des matériaux, CRISMAT, UMR 6508 CNRS, CAEN, France

email: mezaoui_dji@yahoo.fr

The title compound vanadium-tungsten mixed oxide bronze $K_{0.399}V_{2.623}W_{0.377}O_{7.5}$ was prepared by solid state reaction at 700°C in an evacuated silica ampoule. The single crystal $K_{0.399}V_{2.623}W_{0.377}O_{7.5}$ crystallizes in the monoclinic system, C 2/m (n°12) space group, with cell parameters a = 15.7123 (3) Å, b = 3.6796 (6) Å, c = 10.2092 (2) Å and b = 108.994° (4) .This phase is isostructural to $b-K_xV_3O_5$ called: Bannermanite family with x ranging between 0.19 and 0.4.

The idea of this work is to incorporate the vanadium and the tungsten in the same site in order to distort the octahedral polyhedra occupied by the transition metals M (M : vanadium and tungsten elements). The irregular octahedral site is based on the presence of long (M-O) and short bonds (M=O) formed between the transition metal and the oxygen. On the other side, the distortion involves a polarization along the short and long bonds, which can be the origin to improve the electronic delocalization and the no linear optical property. In this context, in 2009 and 2012 we synthesized two single crystals K1.65V1.78W0.22As2O10 (Acta Cryst. (2009). E65, i69) and K₂V₂As₂O₁₀ (Acta Cryst. (2012). E68, i54) isostructural to KTiPO₅. The comparison between the MO6 octahedra (M: 78% of vanadium and 22% of tungsten) of K1.65V1.78W0.22As2O10 and VO6 octahedra of K₂V₂As₂O₁₀, showed clearly a strong distortion in "M" site due to the mixed occupation of vanadium and tungsten simultaneously. Furthermore the mixed occupation creates two short bonds, which can have a strong impact on the no linear optical property.

We are interested in the mixed occupation of vanadium and tungsten to improve the physical properties specially the electronic conduction and the no linear optical property, and explain these physical behavior by the structural arrangement of the atoms. In this context, the electrical conductivity measurement as function of various temperatures ranging (between 400 and 625 K) and frequency (100 - 10^{5} Hz) showed a semi-conductor behavior for $K_{0.399}V_{2.623}W_{0.377}O_{7.5}$. The flexibility of the investigated structure gives the possibility to substitute the potassium ion by another alkaline ion with small size as lithium, in order to create a new material used as a rechargeable electrode in the lithium batteries.

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Keywords: Crystal growth, Structure determination, vanadotungsto oxide, Semiconductor.

Tunable crystal structure and proton conductivity of lanthanide nitrilotrismethylphosphonates

Inés Ruiz Salcedo¹, Aurelio Cabeza Díaz¹, Montse Bazaga García¹, Rosario Mercedes Pérez Colodrero², Gary Hix², Enrique Ramírez Losilla¹, Pascual Olivera Pastor¹

- Departamento Química Inorgánica, Cristalografía y Mineralogía. Facultad de Ciencias. Universidad de Málaga., Málaga, Spain
- Wolverhampton School of Sciences. Faculty of Science and Engineering. University of Wolverhampton., Wolverhampton, United Kingdom

email: inesrs@uma.es

Metal phosphonates are multifunctional solids with remarkable stability and proton conducting properties owing to their structure is usually composed of extended hydrogen-bond networks that favor proton transfer pathways [1]. Moreover, these properties can be enhanced by appropriate modification of the synthesis conditions [2, 3].

In this communication, a new family of isostructural 2D layered compounds based on lanthanide nitrilotris-methylphosphonates is reported. These compounds have been isolated at room temperature and have the general formula Ln[N(CH₂)₃(PO₃H₂)₂(PO₃H)(H₂O)]SO₄·2H₂O (Ln= Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er and Yb). The coordination environment of Ln3+ is composed by eight oxygen atoms from three different ligands and two oxygens from bound waters. This connectivity creates positive charged layers connected to sulfate ions through hydrogen-bonds. These compounds show promising proton conductivity with values ranging between 7.6 · 10-2 and 3.8 · 10-2 S · cm-1 at 80 °C and 95% RH and low activation energy corresponding to Grotthuss-type proton transfer mechanism. In addition, a structural transformation occurs at T > 70 °C accompanied by a remarkable enhanced conductivity. Studies on the structure-properties relationships will be discussed.

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Keywords: metal phosphonates, proton conductivity, crystal structure

MS16-P03

Perovskite-type hybrid materials with lead halide complexes and piperidine methyl derivatives: Design, synthesis and structural analysis

Pawel Socha1, Lukasz Dobrzycki1, Michal K. Cyranski1

1. Department of Chemistry, University of Warsaw, Warsaw, Poland

email: psocha@chem.uw.edu.pl

Perovskite-type halide hybrid salts are intriguing materials. Depending on the size and shape of an organic cation it is possible to obtain 0-D, 1-D, 2-D or

3-D architecture of polymerized inorganic complexes in the crystal structure. Physicochemical properties of these materials strictly depend on this architecture, kind of metal cation and halide anion, what gives many possibilities of modification depending on creators preferences. Therefore, hybrid salts are known as semiconductors, magnetics or solar cell components. [1] [2]

The aim of this project is design, synthesis and structural analysis of new organometallic systems of lead halides – piperidine (and its derivatives). Based on the received results, it is available to propose the rules governing the crystal architecture of the hybrid salts.

Piperidine is a six-membered heterocyclic aliphatic amine, which may be relatively easily modified by substitution e.g. by methyl group in various position(s) in respect to the nitrogen atom. Size of the organic cation should affect crystal structure, because it can fill more space in the unit cell. Additionally, covering of amine group should have influence on structure, because of reduce accessibility atoms to create hydrogen bonds between organic and inorganic part.

Lead halide was chosen as an inorganic part of hybrid material. It is well known that lead halide creates octahedral complex of PbX₆⁻⁴, hence it was expected to receive various motifs of polymerized inorganic complexes like 1-D chains, 2-D layers or 3-D motifs. [1][2][3] Chlorides and bromides was used independently as halides.

During the studies, 9 crystals were obtained. All structures were determined by single crystal x-ray diffraction and additionally characterized by Raman spectroscopy. For systems containing lead bromide, 5 of them exhibit 1-D inorganic chain structure. Structural analysis showed that, few of them are isostructural despite the different position of the methyl group. Moreover, one of them form uncommon 3-D inorganic structure (Fig. 1), what is exception in the examinated series of systems with piperidine derivatives and lead bromide. In contrast to the previous systems, 3 obtained crystals with attention to the influence of the size of used halogen anion.



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Keywords: Hybrid materials, Perovskite-type halides, Crystal engineering

MS16-P04

Pre-transitional processes in lead zirconate doped by Ti studied by diffuse and inelastic X-ray scattering

Daria Andronikova¹, Roman Burkovsky², Yurii Bronwald², Alexei Bosak³, Dmitry Chernyshov⁴, Igor Leontiev⁶, Nikolai Leontiev⁶, Alexey Filimonov², Sergey Vakhrushe¹

- 1. Ioffe Institute, St. Petersburg, Russia
- 2. Peter the Great St.Petersburg Polytechnic University, St. Petersburg, Russia
- 3. European Synchrotron Radiation Facility, Grenoble, France
- 4. Swiss–Norwegian Beamlines at the European Synchrotron Radiation Facility, Grenoble, France
- 5. Southern Federal University, Rostov-on-Don, Russia
- 6. Azov Black Sea Engineering Institute, Zernograd, Russia

email: andronikova.daria@gmail.com

Lead-zirconate titanate (PbZr_{1-x}Ti_xO₃, PZT) is one of the most actively studied and widely used ferroelectric materials. One of the reasons of the interest is a complex phase diagram of lead zirconate and lead titanate solid solution, which illustrates variety of physical properties and crystal structures depending on titanium concentration. Other reasons of popularity are high piezolelectric properties, demonstrated by PZT around morthotropic phase boundary, and prospects of application of antiferrolectric properties [1], demonstrated by PZT with low Ti concentration.

Pure lead zirconate (x=0) is the prototypical antiferroelectric material. Between the cubic perovskite paraelectric phase and the antiferroelectric phase, in the narrow temperature range, intermediate ferroelectric phase exists. Addition of titanium increases the temperature range of stability of this phase. Cubic-to-intermediate phase transition is accompanied by doubling of the cell parameters of the paraelectric cubic lattice along two directions [2] and results in the appearance of M-superstructure with coordinate (H \pm 1/2 K \pm 1/2 0) in the diffraction pattern. Observation of additional satellites around M-point by electron diffraction [2] results in conclusion about complex domain pattern, characterized by antiphase domain boundary in lead displacement.

Recent studies [3] of pure lead zirconate reveals complex pattern of dynamical correlations in paraelectric phase. Diffuse scattering distribution indicates disordering of oxygen octahedral tilts and Pb displacements is shown in the high-temperature cubic phase. To study temperature behavior of these correlations X-ray diffuse scattering measurements have been done in wide temperature range in PZT with small titanium concentration (x < 0.04). To characterize dynamical origin of DS lattice dynamics have been studied using inelastic X-ray scattering. Obtained temperature evolution of DS and pre-transitional dynamical peculiarities will be shown in presentation and discussed in the context of mode coupling.

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Keywords: ferroelectric, lattice dynamics

MS16-P15

Interplay of cation disorder and thermoelastic properties of MgGa₂O₄

Christian Hirschle¹, Jürgen Schreuer¹, Zbigniew Galazka²

- Institute of Geology, Mineralogy, and Geophysics, Ruhr-University Bochum, Bochum, Germany
- 2. Leibniz Institute for Crystal Growth, Berlin, Germany

email: christian.hirschle@rub.de

Transparent semiconducting oxides are materials suitable for a wide variety of optoelectronic applications, such as UV-LEDs, Schottky diodes, high voltage transistors and transparent thin film transistors. Spinel structure MgGa2O4 was recently shown to have an appropriate carrier concentration and bandgap for such applications and it can be grown using various techniques from the melt as relatively large crystals^[1]. Furthermore, it has a high chemo-physical stability and its conductivity can be controlled by adjusting the atmosphere during the growth process^[1], making it an excellent candidate for future applications. However, spinel-like materials often exhibit anomalies in their physical properties at higher temperatures due to changes of their cation ordering (normal/inverse spinel). In fact, both heat capacity^[1] and thermal diffusivity^[2] of MgGa₂O₄ were shown to behave anomalously as a function of temperature.

We studied this issue by direct investigation of the cation ordering of annealed samples using single crystal X-ray diffraction. Additionally, we used inductive gauge dilatometry and resonant ultrasound spectroscopy to determine thermal expansion and the complete set of elastic constants, respectively, from 103 K to 1673 K to assess correlations between the changing structure and properties.

Thermal expansion and most stiffness coefficients show a discontinuity in their temperature dependence at about 820 K. Furthermore, the cation disorder is independent of temperature up to about 820 K and increases gradually at higher temperatures. Thus, the cation disorder in MgGa₂O₄ is most likely in equilibrium at high temperatures and undergoes a transition to a nonequilibrium state below 820 K, where the disorder cannot relax in laboratory timescales; a glass-like transition. This transition is likely also related to the anomalies in heat capacity^[1] and thermal diffusivity^[2]. The bond-valence model can qualitatively explain the relation between changing cation order and thermoelastic properties.

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Keywords: spinel, elasticity, disorder

Structural studies of HS↔LS transition triggered by temperature or laser light irradiation in the [Fe(ebtz)₂(RCN)₂](BF₄)₂ complexes

Joachim Kusz¹, Marcin Kaźmierczak², Maria Książek¹, Miłosz Siczek², Robert Bronisz², Aleksandra Tołoczko², Marek Weselski²

1. Institute of Physics, University of Silesia, Katowice, Poland

2. Faculty of Chemistry, University of Wrocław, Wrocław, Poland

email: kusz@us.edu.pl

Spin crossover in the complexes of $3d^4$ - $3d^7$ metal ions is associated with the change of magnetic, optical and structural properties.¹ In iron(II) complexes the HS \leftrightarrow LS transition is accompanied by shortening of Fe-ligand distance at about 0.2Å. This alteration becomes an origin of perturbation influencing on neighboured molecules as well as spreading through intermolecular interactions on the whole crystal lattice. It can lead to appearance of cooperative behaviours resulting in occurrence of spin crossover in narrow temperature range.

1,2-di(tetrazol-2-yl)ethane (ebtz) creates with iron(II) perchlorate one-dimensional (1D) coordination polymer [Fe(ebtz)₂(C₂H₅CN)₂](ClO₄)₂ exhibiting abrupt spin crossover accompanied by wide hysteresis loop $(T_{1/2}^{\uparrow} \approx 112K)$, $T_{1/2} \approx 141$ K).² The characteristic feature of this complex is uncommon orientation of axially coordinated propionitrile molecules because Fe-N-C(nitrile) angle adopt at 250K value of 149.1(3)°. What is interesting the HS \leftrightarrow LS transition is connected with reorientation of nitrile molecules and in the LS form Fe-N-C(nitrile) angle increases to 162.9(2)°. In order to elucidate a mechanism of spin crossover in [Fe(ebtz)₂(RCN)₂](BF₄)₂ polymers, we have carried out systematic studies changing coordinated nitrile molecules (R = $-CH_3$, $-C_2H_5$, $-C_3H_5$, $-C_3H_7$, $-CH_2Cl$). It was established that the novel complexes crystallize as 1D coordination polymers in which two ebtz molecules link neighbouring Fe(II) ions and axial positions in coordination octahedron are occupied by nitriles. In the complexes containing coordinated molecules of butyro-, allylo- or chloroacetonitrile the HS↔LS transition is accompanied by shortening of the Fe-N distances at about 0.2Å, however, values of Fe-N-C(nitrile) angles remain very similar in both spin forms. In acetonitrile based system the difference becomes more visible. In the HS form Fe-N-C(acetonitrile) angle adopts value of 167.4(2)° (230K), whereas it increases to 171.6(2)° (120K) in the LS form. Unfortunately propionitrile derivative remains in the HS form up to 80 K upon cooling. Therefore in order to determine the crystal structure of the LS form and find the value of Fe-N-C(nitrile) angle we have performed the HS↔LS switching at 15K using laser light irradiation (808nm). We have established that similarly to [Fe(ebtz)₂(C₂H₅CN)₂](ClO₄)₂ formation of the LS form in tetrafluoroborate analogue is associated with reorientation of propionitrile molecule. Detailed results of single crystal X-ray diffraction studies of [Fe(ebtz)₂(RCN)₂](BF₄)₂ (R = -CH₃, -C₂H₅, -C₃H₅, -C₃H₇, -CH₂Cl) complexes in HS and LS forms, generated by change of temperature or as a result of laser light irradiation, will be presented.

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Keywords: spin crossover, Fe(II) complexes

Determination of $L2_1$ vs. B2 phase content in Heusler alloys Ni_2MnGa and $Co_2FeGe_{0.5}Ga_{0.5}$ with x-ray diffraction

Petr Cejpek¹, Daniel Král², Elen Duverger-Nédellec¹, Lukáš Horák¹, Vacláv Holý¹

- Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic
- Institute of Physics of Charles University, Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic

email: petr.cejpek@centrum.cz

Ni₂MnGa and Co₂FeGe_{0.5}Ga_{0.5} are promising members of Heusler alloys because of their application potential. Ni₂MnGa is a shape-memory alloy which can be used for micropumps [1] or actuators [2] and Co₂FeGe_{0.5}Ga_{0.5} has a potential in spintronics [3]. Important properties used for applications are conected to the low-temperature L2₁ phase. The high-temperature B2 phase (assuming the formula X₂YZ, the elements Y and Z are mixed together at their positions in unit cell) is for these purposes parasitic and we need to get rid of it. The presence of B2 phase can be observed for example in as cast samples without further heat treatment.

This work presents the determination of $L2_1$ phase content by x-ray diffraction. According to symmetry, we should observe $L2_1$ phase only diffraction with all indices odd or all even (*fcc* symmetry). Higher symmetry of B2 phase discribed with the equally big unit cell leads to the extinction of diffractions which have all indices odd. Proper computation of structure factors shows that diffractions with all even indices remain the same in both phases. Therefore, the ratio of integrated intensities corresponding to diffractions with all indices odd and all indices even should reveal the content of $L2_1$ phase in the sample. However, the whole problematics is more complicated, because it is neccessary to apply all angularly dependend corrections such as polarisation, Lorentz correction, absorption, irradiated volume and primary and secondary extinction.

The results show that this procedure works fine with thin layers and with bulk single-crystals with small mosaicity. If the mosaicity is large enough, it complicates the application of the corrections – especially the irradiated volume and extinction – because it is unclear how big volume of which mosaic block was irradiated. Extinction correction is connected to the size and misorientation of these blocks. Nevertheless, it is clearly visible that good temperature treatment can increase the L2₁ content, because overall intensity of sensitive diffractions (all indices odd) increases after annealing procedure (diffraction measured in the same experimental arangement for all cases).

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Keywords: Heusler alloys, B2 and L21 phase, intensity corrections

MS16-P08

Thickness distribution of triglyceride crystallites in vegetable fat blends

Ruud den Adel¹, Kees van Malssen¹, John van Duynhoven¹, Oleksandr O. Mykhaylyk², Adrian Voda³

- 1. Unilever R&D Vlaardingen, Vlaardingen, Netherlands (Holland, Europe)
- 2. Department of Chemistry, The University of Sheffield, Sheffield, United Kingdom
- 3. Vlaardingen, Vlaardingen, Netherlands (Holland, Europe)

email: adel03@zonnet.nl

The structure of many food products is based on networks of crystalline particles. In oil-continuous products, such as margarine or butter, this network consists of a mixture of small crystallites of triglycerides (also known as triacylglycerols or TAGs) [1]. Product quality is related to the manufacturing process used, since the growth of the fat crystals can be tuned by TAG composition and cooling rates. For a given composition, fat network formation depends on the amount of TAG crystals and their dimensions and is therefore directly related to the surface to volume ratio.

Small Angle X-ray Scattering (SAXS) measurements were performed on both home-lab equipment (D8-Discover, Bruker-AXS) and at the ID02 beamline at the ESRF, Grenoble to obtain information about the thickness of the fat crystallites (domains). Based on the Full Width at Half Maximum (FWHM) of the first order diffraction line the average crystallite thickness is calculated using the Scherrer equation. However, in order to have a better understanding of the structuring capability of the TAGs, knowledge of the thickness distribution of the crystallites is preferred.

Peak shape analysis based on Fourier transformation methods was performed on the X-ray diffraction patterns. We considered the Bertaut-Warren-Averbach [2] method to be a feasible approach to resolve crystallite thickness distributions (CTD) in TAGs where molecules are packed in repeating bi-layers in longitudinal direction. This method, initially developed for metals, was also successfully applied to obtain distributions of domain thickness of layered clay minerals [3]. The proof of principle of BWA method for CTD in fats is presented on a model system consisting of mono-acid TAG (tripalmitate) subject to shock- and slow-cooling. Examples on real-use mixed-acid TAG systems or so-called fat blends are presented as well.

With additional knowledge of the thickness distribution of triglyceride crystallites it might be possible to tune the fat blend composition and to further optimize the processing of food products.

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Keywords: triacylglycerol, crystallite thickness distribution, Bertaut-Warren-Averbach analysis

Titanyl sulfate dihydrate - template for preparation of 1D titania structures

Mariana Klementova¹, Monika Motlochova², Jaroslav Kupcik², Lukas Palatinus¹, Eva Plizingrova², Lorant Szatmary³, Jan Subrt²

- 1. Institute of Physics of the Czech Academy of Sciences, Prague, Czech Republic
- Institute of Inorganic Chemistry of the CAS, v.v.i., CZ-250 68 Husinec-Rez, Husinec-Rez, Czech Republic
- Nuclear Research Institute, a.s., Hlavní 130, CZ-250 68 Husinec-Rez, Husinec-Rez, Czech Republic

email: klemari@fzu.cz

Titanyl sulfate dihydrate (TSD, TiOSO₄·2H₂O) can serve as a template for preparation of 1D titania structures. When immersed in aqueous ammonia at a temperature of about 0 °C the crystals of TSD provide solid residue composed of particles, whose shape and dimensions correspond perfectly to the rod-like particle morphology of the initial titanyl sulfate with composition matching that of metatitanic acid. When annealed up to 1200 °C, the rod-like morphology of particles is retained, while the phase composition changes to anatase/rutile. To understand the mechanism of the phase transformation that is not accompanied with a change of particle shape, the structure of TSD had to be determined.

The TSD crystals form very thin platelets unsuitable for investigation by single-crystal x-ray diffraction. The structure was therefore solved using dynamical refinement of precession electron diffraction tomography data using PETS [1] and Jana2006 [2].

The structure is monoclinic *Pn* with lattice parameters a = 5.54(2) Å, b = 16.77(9) Å, c = 18.74(10) Å, $b = 90.5(3)^{\circ}$. 54 independent non-hydrogen atoms were easily identified in the electrostatic potential distributionobtained ab initio by charge flipping. To keep charge balance such model requires 24 hydrogen atoms, whose positions were estimated based on the bond-valence calculations [3]. 17 hydrogens out of 24 could be matched to the maxima in the difference map calculated from combined refinement of 6 datasets. The remaining hydrogen positions were estimated based on the knowledge of water molecule geometry. The agreement factor R_{obs} decreased from 10.36 % to 9.89 % after including the hydrogens.

The TSD structure is composed of two symmetry independent helices of corner sharing TiO₆ octahedra extending along a (Figure 1). Each pseudotrigonal helix is held together by SO4 tetrahedra that share corners with odd/even TiO₆ octahedra. Both hydrogens in each water molecule form hydrogen bonds toward oxygens of two different SO4 tetrahedra. One H-bond points to the oxygen of SO4 tetrahedra from the same helix, while the other H-bond points to the oxygen of SO₄ tetrahedra from the neighboring helix. Based on the structure a tranformation mechanism could be proposed. During the reaction the sulfate anion are replaced with OH-. The replacement of sulfate by OH- anions in the helix does not cause a collapse of the helices as the newly bonded OH-groups repel one another. However, the interaction between the helices is weakened, resulting in polymer-like chains of TiO₆ octahedra characteristic for the amorphous metatitanic acid.



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Keywords: electron diffraction, titanyl sulfate dihydrate, pseudomorphs

Determination of the crystal structures of an oxidized TbDy₂Fe₆ thin film by synchrotron radiation anomalous X-ray scattering

Chih-Hao Lee1, Hsinchu, Taiwan1 Wen-Ching Chang1

1. Department of Engineering and System Science, National Tsing Hua University, Hsinchu, Taiwan

email: chlee@mx.nthu.edu.tw

The cubic Laves phase RFe_2 compounds (R= Tb and Dy) with cubic $MgCu_2$ -type structure have giant room temperature magnetostriction constants. To make this compound as a thin film is very useful for the applications on Micro-Electro- Mechanical Systems However, as a thin film, it is apt to the oxidation of the thin film. To study the oxidation of RFe2 thin film is of interesting in the material science.

In this work, 160 nm TbDy₂Fe₆ thin films were prepared by magnetron sputtering and annealed in the range of temperature between 550 and 850 °C. The structure of TbDy₂Fe₆ thin films were characterized by X-ray diffraction, and strong diffraction peaks of rare-earth oxides, Tb₂O₃ or Dy₂O₃ and other non-stoichiometric peaks were found. Since the lattice structure of Tb₂O₃ is very similar to that of Dy₂O₃, the composition of Tb₂O₃ and Dy₂O₃ cannot be determined by XRD separately. By using synchrotron radiation anomalous X-ray scattering, the amount of Tb and/or Dy oxidized at different annealing temperatures was determined. In addition, a pure Fe peak (110) was also detected using XRD. We use the anomalous X-ray diffraction and electron probe micro-analyzer to study this Fe diffraction peak.

With the anomalous X-ray scattering, the composition of the Tb_2O_3 or Dy_2O_3 was found to be the same as the sputtering target materials. It might be due to the same formation energies of oxides of Tb and Dy. In addition, 600 nm Fe clusters phase segregated from the bulk matrix without oxidation was also identified. These pure Fe cluster without oxidation might be due to the protection effect of Gd and Tb matrix.

In conclusion, oxidation of TbDy₂Fe₆ thin films were studied by X-ray anomalous scattering. The composition of Tb₂O₃ and Dy₂O₃ are similar to the composition of sputtering target. In addition, the Fe clusters phase segregated from the bulk matrix without oxidation was also identified.

Keywords: TbDy2Fe6, oxidation, anomalous X-ray scattering

MS16-P11

Structure- property relations and structural instabilities in high-temperature piezoelectric rare-earth calcium oxoborates *R*Ca₄O(BO...

Marie Münchhalfen¹, Jürgen Schreuer¹, Christoph Reuther², Jens Götze², Erik Mehner³, Hartmut Stöcker²

- 1. Institut für Geologie, Mineralogie und Geophysik, Ruhr-Universität Bochum, Bochum, Germany
- Institut f
 ür Mineralogie, TU Bergakademie Freiberg, Freiberg, Germany
- 3. Institut für Experimentelle Physik, TU Bergakademie Freiberg, Freiberg, Germany

email: marie.muenchhalfen@rub.de

Monoclinic (space group Cm) rare-earth calcium oxoborates (*RCOB*), *R*Ca₄O(BO₃)₃ (R = rare earth element), have been studied for about 25 years because of their promising non-linear optical properties. These crystal species are isostructural with calcium fluoroborate, Ca₅(BO₃)₃F [1], whose structure in turn is closely related to the one of hexagonal fluorapatite [2]. The substitution of tetrahedral PO₄ groups by planar BO3 groups causes distortions which is the reason for the pronounced polar properties of the rare-earth oxoborates. Recently, the members of the RCOB family gathered interest as potential candidates for high-temperature piezoelectric sensing applications since they combine favorable properties like high melting point at around 1770 K, no reported structural phase transitions, high piezoelectric sensitivity and high electric resistivity [3]. Furthermore, the RCOB structure offers different possibilities for cation substitution which in principle allow for tuning of physical properties. Their low symmetry results in a high number of degrees of freedom regarding the anisotropy of physical properties.

We studied heat capacity, thermal expansion as well as dielectric, piezoelectric and elastic properties of GdCa₄O(-BO₃)₃ between 100 K and 1473 K using differential scanning calorimetry, dilatometry and resonant ultrasound spectroscopy. Contrary to the reported lack of phase transitions, all investigated physical properties undergo reproducible discontinuities at around 1000 K. X-ray diffraction experiments on quenched samples indicate a gradual increase of cation disorder starting roughly at around 1000 K. Therefore, a glass-like transition from static to dynamical cation disorder is likely responsible for the observed discontinuities. First results indicate only a minor influence of the glass-like transition on the electromechanical properties.

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Keywords: piezoelectricity, elasticity, order-disorder

Dielectric, pyroelectric and structural properties of rare-earth calcium oxoborates *R*Ca₄

Erik Mehner¹, Hartmut Stöcker¹, Marie Münchhalfen², Christoph Reuther¹, Jens Götze¹, Jürgen Schreuer², Dirk C. Meyer¹

1. TU Bergakademie Freiberg, Freiberg, Germany 2. Ruhr Universität Bochum, Bochum, Germany

email: erik.mehner@physik.tu-freiberg.de

Although rare-earth oxoborates are known since 1991 [1], they have been studied mainly for their non-linear optical properties that are useful for Laser applications. Recently, these materials gathered interest due to their piezoelectric properties, which are not only stable up to high temperatures [2], but also unimpaired by phase transitions. Furthermore, the materials lend themselves to rare-earth substitution, thus, offering a systematic possibility to tweak their properties. However, the low symmetry of their monoclinic structure of space group Cm complicates characterisation. Here, we report on the dielectric and pyroelectric properties of some rare-earth calcium oxoborates and present high-temperature powder diffraction data giving insight into possible structural instabilities around temperatures of 1000 K.

Samples of rare-earth calcium oxoborates RCa2Ca2O(-BO3)3 with R = Gd, Y, Er, La were cut and polished from large Czochralski-grown single-crystals. The four components of the dielectric tensor were investigated at room temperature with the substitution method. Furthermore, the two components of the pyroelectric tensor were measured via the Sharp-Garn method from room temperature to 420 K. The stability of noble metal electrodes was investigated up to 1200 K.

High-temperature X-ray powder diffraction patterns obtained on samples milled from crystals exhibit a discontinuity in the expansion of the crystal lattice at elevated temperatures for R = Gd, La, Y, Sm. Comparing the initial and final diffraction patterns reveals changes in the cation ordering due to the thermal treatment.

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Keywords: borate dielectric pyroelectric

MS16-P13

Insertion/disinsertion of oxygen in $BaCoO_{2+x} (0 \le x \le 1)$

Aliou Diatta1, Pascale Armand1, Jérôme Rouquette1

1. Institut Charles Gerhardt, Montpellier, France

email: aliou.diatta@umontpellier.fr

The crystal structure of BaCoO₂ was determined for the first time by Spitsbergen [1] in 1960. Despite the absence of experimental structural data, it was reported to crystallize in the non-centrosymmetric $P3_121$ trigonal space group (no. 152), similar to that observed for SiO₂ quartz, which has potential piezoelectric properties. The screw axis of this trigonal unit cell is defined by the arrangement of corner-sharing CoO₄ tetrahedra around the barium atom, which is located in a distorted 8-fold (4+2+2) oxygen atoms coordination (fig).

The 3d⁷ electron configuration of the tetrahedral Co²⁺ ion exhibits a theoretical effective magnetic moment $\mu_{eff} = 3.87\mu$ B. The existence of this magnetic moment associated with the *P*₃₁21 space group permits potential piezo-magnetic coupling [2].

The BaCoO₂ phase was synthesized by the solid state reaction under secondary vacuum and its structural changes as a function of temperature were studied as the function of oxygen partial pressure. BaCoO₂ presents antiferromagnetic ordering at room temperature and crystallizes in the P3121 space group which confirms potential piezo-magnetic coupling. In addition, oxygen insertion/disinsertion over an extended compositional range was characterized in BaCoO_{2+x} (O \leq x \leq 1) by thermogravimetric analysis (TGA), X-ray diffraction (XRD) and Raman spectroscopy.

Such properties could be of interest for catalysis applications, commercial air separation, solar water splitting, solar CO_2 splitting, chemical looping, oxy-combustion, [3], etc...



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Keywords: Synthesis, Magnetism, Piezomagnetism

MS16-P14

A bi-porous metal–organic framework with tuneable sorption performance facilitated by intrinsic flexibility

Andrzej Gładysiak¹, Kathryn S. Deeg², Iurii Dovgaliuk³, Kaili Y. Ordiz⁴, Seyedmohamad Moosavi¹, Daniele Ongari¹, Jorge A. R. Navarro⁵, Berend Smit¹, Kyriakos C. Stylianou¹

- Laboratory of Molecular Simulation (LSMO), Institut des sciences et ingénierie chimiques (ISIC), École polytechnique fédérale de Lausanne (EPFL) Valais, Sion, Switzerland
- 2. Department of Chemistry, University of California, Berkeley, United States of America
- 3. Swiss-Norwegian Beamlines, European Synchrotron Radiation Facility, Greboble, France
- Department of Chemical and Biomolecular Engineering, University of California, Berkeley, United States of America
- 5. Departamento de Química Inorgánica, Universidad de Granada, Granada, Spain

email: andrzej.gladysiak@epfl.ch

Efficient CO₂/CH₄ separation has constantly been a challenge for natural gas processing, and in general, modern chemical industry.[1] While classical separation techniques including cryogenic distillation or low-temperature chemical absorption are widely in use, they are energetically costly, and present a considerable environmental issue.[2] Porous materials, constantly developed as alternative solutions to these techniques, are showing a great promise.[3] The purpose, however, is not only to design a material with maximum selectivity and working capacity, but also to rationally control and tune its performance. Herein we present the synthesis of a novel MOF based on Ca(II) and a tetracarboxylate ligand TBAPy4endowed with two chemically distinct types of pores: the hydrophobic and the hydrophilic one. Owing to judicious choice of conditions access is gained to two stages of activation, at which the material shows strikingly different gas sorption performances. The material's intrinsic flexibility helps it to adsorb a higher amount of gas molecules than is allowed by its unexpanded state. The observed preference of adsorbing CO2 over CH4 was further studied in fixed-bed breakthrough experiments imitating the real process in an industrial-scale installation. The difference of sorption behaviour on the material was supported by molecular simulations.



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Keywords: metal–organic frameworks, gas adsorption, CO₂/ CH₄ separation

Assessment of Pyroelectricity in Polar Oxides from Atomic Displacements

Tina Weigel¹, Matthias Zschornak¹, Claudia Funke¹, Sven Jachalke¹, Carsten Richter², Melanie Nentwich¹, Hartmut Stöcker¹, Tilmann Leisegang¹, Dirk C. Meyer¹

- 1. TU Bergakademie Freiberg, Insitut of Experimental Physics, Freiberg, Germany
- 2. Eurpoean Synchrotron Radiation Facility (ESRF), Grenoble, France

email: tina_weigel90@web.de

The phenomenon of pyroelectricity is known since 2000 years and describes the temperature dependency of the spontaneous polarization in non-centrosymmetric crystals. The origin is based on displacements of the atomic positions induced by temperature variations. These structural changes are measurable with common structural analysis methods, *e.g.* single crystal X-ray diffraction (XRD). However, in addition electron density redistributions play a crucial role.

This work shows an approach how to use measurable structural changes in combination with electronic structure modeling to determine pyroelectric coefficients of materials. Atomic displacements have been determined with XRD for the crystal structures of the pyroelectric standards and well-known material systems lithium niobate (LiNbO3) and lithium tantalate (LiTaO3) in a temperature range from 80 K to 400 K. As a result, the spontaneous polarization and the pyroelectric coefficient have been calculated and show a high comparability with theoretical and experimental data. Furthermore, the newly developed Resonant X-ray Diffraction method REXSuppress [Richter2018] provides increased sensitivity for very small displacements of the atoms. Hereby, destructive interference of the intensity at specific Bragg reflections is used to detect structural deviations at picometer accuracy. This is particularly important for tiny structural changes, as shown for the recently discovered pyroelectric migration-induced field-stabilized polar (MFP) phase in normally non-polar cubic strontium titanate (Sr-TiO₃) [Hanzig2013, Hanzig2015].

This work may be of wide interest for the pyroelectric community, presenting an alternative approach to determine pyroelectric properties from structural data and for the characterization of structural and physical properties of new materials or phases.

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Keywords: atomic displacement, pyroelectricty, structureproperty-relation

MS16-P16

Crystal structur

Milica Milosavljevic1, Yuri Grin2, Horst Borrmann2

- 1. Max-Planck-Institut fuer Chemische Physik fester Stoffe, Dresden, Germany
- 2. Max Planck-Institute for Chemical Physics of Solids, Dresden, Germany

email: milicamilosavljevic87@gmail.com

In course of extensive investigations of the Al - Cr phase diagram AlCr2 was commonly assigned as Cr-richest binary compound, however, stable below about 900°C only [1]. Based on powder diffraction data MoSi2 structure type was assigned, but no detailed structural analysis has been described till now. The phase diagram is indicating particular problems to obtain single crystals of this particular intermetallic compound. In a multi-step sintering procedure, carefully monitored by powder diffraction as well as scanning electron microscopy (SEM), finally well-defined samples were obtained. Within these samples large grains measuring up to 100 µm could be identified and selected ones were cut out using focused-ion beam (FIB) methods. Those pieces proved to be single crystals with good quality and allowed for the first detailed structural investigation of AlCr₂. Lattice parameters a = 3.0056 and c = 8.6449 Å for the body-centered tetragonal unit cell are in excellent agreement with those given in [1] for the ideal composition. The structural model refines well in space group I4/mmm without indications of mixed or anti-site occupancies. The c/a ratio at 2.876 is much larger than the typical value for MoSi₂ at 2.437 and quite close to the ideal value for a threefold bcc-type superstructure. The disordered solid solution of Al in Cr existing at higher temperatures adapts indeed a bcc-type structure. A detailed comparison with the structure of MoSi₂ is currently hampered by the fact that structural parameters given by different authors are varying quite significantly [2, 3].

In an optional way the structural arrangement may be discussed on the basis of hexagonal $AlCr_2$ layers, which are stacked in *ABAB* sequence along [110] direction. This allows for interesting comparison with hexagonal CrSi₂ and orthorhombic TiSi₂ type arrangements in which the same type of layers is stacked in *ABCABC* or *ABCDABCD* sequence, respectively.

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Keywords: intermetallic compound, single crystals, AlCr₂

Pure gyrotropic phase transitions in the arcanite related materials $PbMGeO_4$ (M = Ba, Sr)

Gwilherm Nenert

1. Application Competence Center, Almelo, Netherlands (Holland, Europe

email: g.nenert@gmail.com

Gyrotropic phase transitions are characterized by the appearance of a spontaneous optical activity [1]. The appearance of such activity is very common in ferroelectric materials. In such materials, the optical activity is a second-ary order parameter and is coupled to the primary order parameter which is the electrical polarization. However, only very rare examples are known of a pure gyrotropic phase transition. Among those, one can cite BiFeO₃ under strain [2], $(C_5H_{11}NH_3)_2ZnCI_4$ as function of temperature [3]. In both cases, the transition exhibits a change from Pnma to P2,2,2, symmetry.

In this contribution, we have investigated 2 materials belonging to the BaNdGaO₄ structural type, namely Pb-BaGeO₄ and PbSrGeO₄ using powder X-ray diffraction as function of temperature. While PbBaGeO₄ exhibits a first order phase transition from P2₁2₁2₁ to Pnma symmetry. This behaviour is similar to the one reported for $(C_5H_{11}NH_3)_2Zn-Cl_4$. However, PbBaGeO₄ exhibits phase coexistence and competition over a wide temperature range of about 200°C. On the contrary, PbSrGeO₄ shows a 2nd order type phase transition towards a Pnma structure with nearly metrically hexagonal cell.

This work demonstrates that both materials are purely gyrotropic and identify BaNdGaO₄ structural type as a new source for such materials. Furthermore, those phase transitions seem unusual in light of the complex behavior reported here for these 2 compounds.



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Keywords: gyrotropic, piezolectric, arcanite

MS16-P18

Structural studies of titanium and zirconium silicate ion-exchange materials for the treatment of nuclear waste

Jennifer Readman¹, Nazesh Sajjad², Reece Hall², Phillippa Patterson²

- 1. School of Physical Sciences & Computing, University of Central Lancashire, Preston, United Kingdom
- Structural studies of titanium and zirconium silicate ion-exchange materials for the treatment of nuclear waste., Preston, United Kingdom

email: jereadman@uclan.ac.uk

Zeolites are commonly used as ion-exchange materials for the remediation of nuclear waste, however, they have certain drawbacks. Unlike zeolites which contain SiO₄ and AlO₄ tetrahedra, microporous Ti-silicates can contain SiO₄ tetrahedra and TiO₆ octahedra and therefore structures are possible which have no traditional aluminosilicate analogues. Microporous Ti-silicates such as sitinakite KNa₂Ti-4Si₂O₁₃(OH)·4H₂O and the synthetic niobium doped analogue are used for the removal of Cs' and Sr²⁺ from nuclear waste ^[1]. The work presented here will focus on the structures and thermal behaviour of the ion-exchanged Ti- and Zr-silicates. A clear understanding of both is fundamental in determining if these materials have potential as ion-exchangers within the nuclear industry.

Umbite is a naturally occurring small pore microporous Zrsilicate, found in northern Russia and synthetic analogues, K₂ZrSi₃O₉·H₂O, can be prepared in the laboratory ^[2]. It has an orthorhombic cell with a = 10.2977(2)Å, b = 13.3207(3)Å and c = 7.1956(1)Å. Rocha and co-workers found that synthetic umbite undergoes a topotactic transformation when heated 910°C forming a new microporous Zr-silicate with the formula K2ZrSi3O9·2H2O^[2]. In contrast they found that the Na-exchanged analogue transforms to wadeite and the Cs-exchanged form retains the umbite structure when heated to the same temperature. Ion-exchange studies here have shown that umbite has a preference for common radionuclides, such as Cs+ and Sr2+ and Ce4+ (as a surrogate for Pu), even in the presence of competing ions. In-situ studies show that these materials behave differently with temperature, indicating that the nature and location of the charge balancing cation plays an important part in determining which high temperature phases are formed and the phases formed do not fit either the AV-15 or wadeite structures previously reported.

Natisite is another material which has interesting ion-exchange chemistry and is a layered Ti-silicate with the formula Na₂TiSiO₃^[3]. The structure consists of square pyramidal titanium, with the sodium cations located between the layers. This coordination environment is highly unusual for Ti. It crystallises in the tetragonal space group P4/*nmm*, with a = b = 6.4967(8)Å and c = 5.0845(11)Å Inclusion of zirconium or vanadium in the framework has a considerable effect on the ion-exchange properties, with changes in the exchange capacity and the rate of uptake for certain ions of interest.

A combination of techniques to probe long and short range order (PDF and XAS) have been used to understand the ion-exchange and thermal behaviour of these materials.

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Keywords: Zeotype, ion-exchange, silicate

MS16-P19

Influence of Microstructure on Symmetry Determination of Piezoceramics

Manuel Hinterstein¹, Henry E. Mgbemere², Markus Hoelzel³, Esmaeil Adabifiroozjaei⁴, Charles Sorrell⁴, Mark Hoffman⁴

- 1. Institute for Applied Materials, Karlsruhe Institute of Technology, Karlsruhe, Germany
- Department of Metallurgical and Materials Engineering, University of Lagos, Lagos, Nigeria
- 3. Heinz Maier-Leibnitz Zentrum, Technische Universität München, Garching, Germany
- 4. School of Materials Science and Engineering, UNSW Australia, Sydney, Australia

email: m.hinterstein@kit.edu

Frequently symmetry determination in studies is based on the discussion of agreement factors or the quality of the refinements, rather than on the basis of physical arguments. Especially in the field of piezoceramics this can be observed in the discussion whether monoclinic symmetry can be observed or not.

In this study we could show with temperature-dependent high-resolution X-ray and neutron diffraction that based on agreement factors alone the physical origin of observations cannot be revealed. Only in combination with additional electron microscopy and electron probe microanalysis we could elucidate that a segregation of substituents results in a complex reflection splitting and phase coexistence that can be misinterpreted as monoclinic symmetry. This single-phase monoclinic Pm model is able to perfectly reproduce the diffraction patterns and is known from literature [1,2]. A model with phase coexistence of two classical orthorhombic Amm2 phases can reproduce the diffraction data with equal accuracy.

This demonstrates the need of comprehensive analyses with complementary methods to cover a broad range of length scales as well as considering both average and local structure. The conclusions drawn from this work will have an impact on a broad range of research areas where inhomogeneities cannot be ruled out. The underlying mechanisms of the extraordinary properties of some functional materials originate not just in their structures but also their complex microstructures. Consequently, knowledge of both features of materials may be essential for the exploitation and development of their functionalities as well as improvement of material properties.

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Keywords: piezoelectric, ceramics, ferroelectricity

Crystallization of carbonate minerals in organic matrices: Influence of hydrogel strength and magnesium doping on hydrogel-mineral organization in the mesocrystal composites

Erika Griesshaber¹, Lurdes Fernandez Diaz², Fitriana Nindiyasari³, Xiaofei Yin¹, Martina Greiner¹, Andreas Ziegler⁴, Wolfgang W. Schmahl¹

- 1. Department of Earth and Environment Sciences, LMU Munich, Munich, Germany
- 2. Instituto de Geociencias, Universidad Complutense Madrid , Madrid, Spain
- 3. NRG, Le Petten, Netherlands (Holland, Europe)
- 4. Center for Electron Microscopy University of Ulm, Ulm, Germany

email: E.Griesshaber@lrz.uni-muenchen.de

Mineralized structures generated under biological control are functional tissues and are recognized as prototypes for man-made materials. Biological hard tissues are hierarchical composites and comprise two distinct components: compliant biopolymers that are reinforced by stiff carbonate and/or phosphate minerals.

In order to understand the composite nature and architecture of biologically mineralized hard tissues we conducted biomimetic crystal growth experiments in hydrogel matrices using the double diffusion experimental set-up. We characterized the obtained hydrogel-carbonate composites with FE-SEM, XRD, Rietveld analysis, micro-Raman spectroscopy, electron backscatter diffraction (EBSD). We investigated for two different hydrogels (gelatine, silica) the effect of gel solid content variation in Mg-bearing and Mg-absent growth environments on gel occlusion, gel distribution within the composite aggregate, hierarchy formation for the gel and the mineral and gel fabric and carbonate crystal organization (1, 2, 3, 4). Even though being artificial polymers, hydrogels mimic to some extent biogenic matrices, as they compartmentalize space, thus control, diffusion rates, local concentration of solutes and supersaturation. As each hydrogel has different chemical characteristics, they act differently in promoting or inhibiting crystallization.

We show that gelatin gel exerts most, while silica gel the least influence on calcite organization and aggregate formation (Figure 1). Irrespective of their solid content, all aggregates incorporate gel, which is inhomogenously distributed within the mineral. The mineral fraction in the aggregates is present in a mosaic and mesocrystal constitution. The presence of Mg2+ adds complexity to the internal structuring of the mineral. We show that two independent mechanisms are responsible for the impact of Mg2+ on composite organization. (1.) Addition of Mg²⁺ reduces the yield-strength of the gels by about 50%. While gelatin gel shows continuous strain hardening, silica-gel weakens after reaching a shear strength maximum; the strain shifts by 350% to higher values. (2.) Incorporation of Mg2+ in the growing calcite increases its solubility, decreases crystallization pressure and introduces small angle grain boundaries that leads to split growth and ultimately to spherulitic growth. We show that Mg not only influences the organization of the mineral but also the structure of the gel matrix within the aggregates. With increasing Mg content the gel structure within

the mineral changes from compact gel membranes to finely dispersed networks of gelatine fibres. This induces the large variety of calcite crystal co- and misorientation patterns in the investigated composites. We obtain a wide range of material design principles with some matching features of functional biological hard tissues.



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Keywords: Biomimetic composites, material properties, mesocrystals

Synthesis and properties of puninite-type $A_2Cu_3O(SO_4)_3$ (A = Na, K, Rb, Cs) sulfate materials

Diana Nekrasova¹⁻² Zhuici Chen¹, Vadim Kovrugin³, Olivier Mentré², Marie Colmont², Oleg Siidra¹⁻⁴

- Department of Crystallography, St. Petersburg State University, St. Petersburg, Russia
- Unité de Catalyse et Chimie du Solide (UCCS), UMR 8181, Université Lille, St. Petersburg, Villeneuve d'ASCQ, France
- Laboratoire de Réactivité et de Chimie des Solides (LRCS), UMR 7314, Université de Picardie Jules Verne, Amiens Cedex, France
- Nanomaterials Research Center, Kola Science Center, Russian Academy of Sciences, St. Petersburg, Apatity, Murmansk Region, Russia

email: st014844@student.spbu.ru

Mineral puninite, Na₂Cu₃O(SO₄)₃ was described recently [1] in fumaroles of Tolbachik volcano.

Crystal structure of puninite is based on oxocentered $[O_2Cu_6]^{8+}$ dimers. Four sulphate tetrahedra are 'face-to-face' attached to the dimers, whereas the other sulphate tetrahedral groups provide their linkage in two dimensions. Structural architecture of puninite can be described as being organized via a "host-guest" principle.

Five new compounds with the general formula A_2 Cu₃O(-SO₄)₃ (A =Na, K, Na/K, Rb, Cs) were obtained by solid-state reactions using anhydrous reagents A_2 SO4 (A =Na, K, Rb, Cs), CuSO₄ and CuO mixed in the stoichiometric ratios. The reaction mixture was loaded into platinum crucibles, and kept at 600 °C for 3 h in air, followed by cooling to 25 °C at a cooling rate of 10 °C/min. The products consisted of green crystals of different shape. Pure powder sample of Na₂Cu₃O(SO₄)₃ was prepared for the investigation of magnetic properties, electrochemistry, IR spectroscopy and thermal behavior by the means of HT powder X-ray diffraction and DSC-TGA.

The Na₂Cu₃O(SO₄)₃ phase as a positive electrode was tested using Swagelok-type cells cycled at room temperature. The difficulties of electrochemical Na⁺ extraction have been encountered, and the removal of significant amount of sodium ions from the structure of the title compound was failed. Note, however, that our tests revealed an occurring of a probable redox process corresponding to the Cu^{2+/3+} transition at high voltage of around 4.8 vs Na^{*}/Na.

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Keywords: sulfate, X-ray diffraction

MS16-P22

How heating and surface finishing affects the crystalline and mechanical properties of CAD-CAM dental lithium disilicate glass-ceramic

Javier García-Mira¹, Giordana P. Furini², Paula Benetti², Pedro Álvarez-Lloret¹, Oscar E. Pecho²

- 1. Department of Geology. University of Oviedo, Oviedo, Spain
- Faculdade de Odontologia. Universidade de Passo Fundo, Passo Fundo, Brazil

email: uo252650@uniovi.es

The crystalline characteristics of a dental lithium disilicate glass-ceramic (LDGC) determine the esthetics, strength, and applicability of this material in clinical procedures. The computer-aided design and computer-aided manufacturing (CAD-CAM) technique and heat treatments (temperature, pressure and time) precisely controls the material properties of a LDGC during the manufacturing of dental restorations. During clinical manipulation, finishing and polishing procedures have to be performed on dental restorations. These procedures may affect the topography and modify the microstructural properties of dental ceramics. In the present study, the effect of final crystallization and different finishing and polishing procedures on crystalline and mechanical properties of LDGC were analyzed. For this purpose, the crystalline properties of the LDGC (IPS e.max CAD, Ivoclar Vivadent) were evaluated using 1D and 2D X-ray diffraction (XRD) analyses. The 1D-XRD analyses were performed with an X'Pert Pro (PANalytical) powder diffractometer while 2D-XRD patterns were obtained using an X-ray single crystal diffractometer (Bruker D8 VENTURE) equipped with an area detector (PHOTON100). The crystallization mechanism after heat treatment resulted in a conducted transformation process of the material microstructure. Thus, lithium metasilicate (LM) crystals are transformed into lithium disilicate (LD) crystals. The crystallite size, representing the average coherent crystal diffraction domains, were determined as a crystallinity index for LM and LD crystals after final crystallization. This parameter can be also influenced by the chemical composition of the material aimed for specific clinical purposes. The degree of crystallinity (i.e. crystalline to amorphous) was also obtained by 1D-RXD analyses using the ratio of the intensity of the crystalline peaks to the total intensity in the diffraction pattern, including the signal corresponding to the glass component from the ceramic. The 2DXRD patterns showed a randomly orientation of crystals in both pre and post crystallization during heating. These XRD analyses were also complementary with the results obtained by SEM observations. The increment on the crystallite size and crystal orientation during heat treatment could allow the lower presence and size of voids (densification of the material) that could be acted as potential locations for cracks or affect the optical properties of the material surface. Furthermore, finishing and polishing protocols of ceramic dental restorations differently affect the texture of the material surface, resulting in changes on the flexural strength of the restoration. Overall, translucency and mechanical properties of the lithium disilicate glass-ceramic may be influenced by the crystalline properties of the glass-ceramic during final crystallization and finishing and polishing procedures.

Keywords: dental ceramics, x-ray diffraction, silicate crystals

1:3 A-site ordering in perovskite structures: group theoretical analysis

Mikhail Talanov¹

1. Southern Federal University, Rostov-on-Don, Russia

email: tmikle-man@mail.ru

The quadruple perovskites AA'₃B₄O₁₂ are characterized by an extremely wide variety of intriguing physical properties, which make them demanded for various applications [1,2]. Using group-theoretic analysis, we found all possible 1:3 A-site ordered low-symmetry phases, which can be formed from a parent Pm-3m perovskite structure (archetype) as a result of real or hypothetical (virtual) phase transitions due to different structural mechanisms (ordering and displacement of atoms, anion octahedral tilts). For each of the low-symmetry phases, the complete condensate of order parameters (proper and improper order parameters), the calculated structure, including the space group, the primitive cell multiplication, the distribution of atoms over the Wyckoff positions and the structural formula were determined. All phases were systematized according to the types of structural mechanisms responsible for their formation, and the group-subgroup relations between the phases were investigated. Special attention is paid to the structural mechanisms for the low-symmetry phase's formation of the compounds known from experimental data, such as: CaCu-₃Ti₄O₁₂, CaCu₃Ga₂Sn₂O₁₂, CaMn₃Mn₄O₁₂, Ce_{1/2}Cu₃Ti₄O₁₂, LaMn₃Mn₄O₁₂ and others. For the first time, the variability in the choice of the proper order parameters, which generate 1: 3 A-site ordered low-symmetry phases, highlights the fundamental significance of the complete condensate of the order parameters in the description of structural phase transitions. The constructed map of the 1:3 A-site ordered quadruple perovskites can be used to identify new phases and interpret experimental results, determine the structural mechanisms responsible for the formation of low-symmetry phases as well as to understand the structural genesis of the perovskite-like phases. The obtained non-model group-theoretical results in combination with crystal-chemical data and first principles calculations can be a starting point for the design of new functional materials with a perovskite structure

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Keywords: quadruple perovskites, group-theoretical analysis, order parameter

MS16-P24

Crystallographic studies of NaZr₂(PO₄)₃ phosphates at high temperatures

Albina Orlova¹, Sergei Khainakov², Aleksey Alexandrov¹, Santiago Garcia-Granda², Dmitrii Savinykh¹

- 1. Lobachevsky State University of Nizhni Novgorod, Nizhni Novgorod, Russia
- 2. University of Oviedo, Oviedo, Spain

email: albina.orlova@inbox.ru

Crystal-chemical principles have been used in this paper for modeling of the compositions of NaZr₂(PO₄)₃ compounds and solid solutions with adjustable thermal expansion characteristics. Knowledge about materials on their base helps to solve many engineering problems associated with the combination of materials in different designs, including the required resistance to thermal stress.

 $NaZr_2(PO_4)_3$ (NZP) is a convenient structure for these aims as it offers an opportunity to include a big variety of cations in different combinations with oxidation states from +1 to +5, with different size and electronegativity into the composition of isostructural phases.

Well-known NZP materials have high melting temperatures, high hardness, thermomechanical, radiation, and chemical stability, ion conductivity, optical and magnetic properties, catalytic activity.

Although many of the possible formula compositions calculated in [1] are well studied, but those that have their thermal expansion characteristics determined are quite few.

In this paper new phosphates $Na_{1+2x}Zr_{2-x}Co_x(PO_4)_3$ and $Ca_{0,5+x}Zr_{2-x}Co_x(PO_4)_3$ ($0{\leq}x{\leq}0,5$) in various concentration combinations of zirconium and cobalt in the structure framework and with respectively changing population density of interframe positions are obtained and characterized, their behavior during heating through high-temperature XRD is studied for T=25–700°C.

Synthesis of powder samples was carried out using solid-phase processes ($T_{final} = 700$ °C). The forming of phases of a planed composition and structure were established by XRD and SEM methods. Lattice parameters of the obtained materials were determined and their dependencies on the composition and temperature were analyzed.

It was found that with the temperature rising, *a* and *b* parameters were decreased, while *c* parameter was increased, which is typical for NZP structure. With cobalt growing in the phase composition, absolute values of thermal expansion linear coefficients were decreased: a_a from -4,65·10⁶ to -3,06·10⁶ °C⁻¹, a_c from 21,85·10⁶ to 19,49·10⁶ °C⁻¹ for Na-containing series, a_a from -1,82·10⁶ to -1,14·10⁶ °C⁻¹, a_c from 9,20·10⁶ °C⁻¹ for Ca-containing series and anisotropy: Δa from 26,50·10⁶ to 21,55·10⁶ °C⁻¹ for Na-containing series, from 11,02·10⁶ to 10,24·10⁶ °C⁻¹ for Ca-containing series.

Analysis of the obtained results shows that the phosphates studied belong to the class of medium-expanders ones.

The studied objects have blue color. This property is useful for heat-resistant inorganic dyes applied as a cover on the material, as well as for imparting a functional color to the material itself. The study has been performed with the financial support of the Russian Science Foundation Grant No. 16-13-10464.

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Keywords: NZP, thermal expansion

MS16-P25

Effect of crystallography on the calculation energies of equilibrium and enthalpies of formations at first principles calculations (D.F.T)

Ferroudj abdelhak1, Y. Djaballah1, Dj. Belbacha1

1. Laboratoire d'Etudes Physico-Chimique des Matériaux (L.E.P.C.M) Batna 1 University, Batna, Algeria

email: ferroudjabdelhak@yahoo.fr

Equilibrium energies and enthalpies of formations are calculated based on structural crystallography. Elements and alloys having a large number of atoms are difficult to be compute by density functional theory (DFT): time computation, points of high symmetry.

We have calculated the structural properties, the formation enthalpies and total energies of elements Si, Ni and Au-Re binary compounds (Re = Y, La,Eu) using the first principles calculations based on the density functional theory (DFT) byVasp package.

Comparison of structural properties, formation enthalpies and total energies obtained using firstly the primitive unit cell and secondly the Conventional unit cell of the same phase present a good agreement between the two cases.

The benefits of crystallography allowed the abintio simulator to save computing time; by the exact determination of the atomic positions and symmetry space group of such a material.

Keywords: crystallography, first principles calculation ,enthalpies formation

Revisesd Jiang model's «New formula of Prediction of lattice constant in cubic perovskites»

Krarcha Hadda1, Fatih hamizi2

1. Department of earth sciences, university batna 2, Batna, Algeria

2. Department of physics, batna, Algeria

email: krarcha1974@gmail.com

ABX₃ Perovskite materials are of great interest in the new technology because of the possibility of modifying their physical properties by numerous ionic substitutions.

The mesh parameter prediction model used is useful for providing the predicted structural information for estimating the physical properties of materials for which accurate structural data are not available.

It is also useful as a guide for synthetic exploratory efforts as a starting point for structural characterization improvements of new materials.

Our reformulation of Jiang's model allowed us to obtain a new equation of parameter prediction of cubic perovskite structures taking into account 158 materials.

The results obtained are in good agreement with the experimental with a relative error of the order of 2.64%.

This prediction equation allowed us to predict the mail parameter of 20 new perovskite oxides.

Keywords: mail parameter prediction, cubic perovskite, tolerance factor.

MS17- Biominerals and bioinspired materials

Chairs: Prof. Wolfgang Schmahl, Dr. Anna Schenk

MS17-P01

Removal of methylene blue by adsorption using modified hydroxyapatite by carrageenan biopolymer

Mongi Debbabi¹, Hassen Agougui¹, Mahjoub Jablib², Hatem Majdoub³

- Laboratoire de Physico-chimie des Matériaux, Faculté des Sciences., Monastir, Tunisia
- 2. Textile Materials and Process Research Unit, ENIM, Monastir, Tunisia
- Laboratoire des Interfaces et des Matériaux Avancés, Faculté des Sciences., Monastir, Tunisia

email: m.debbabi@yahoo.fr

The application of hydroxyapatite modified by biopolymers for the immobilization of various pollutants has been considered as a promising pollution control technology. In this scope, hydroxyapatite-Lambda carrageenan CaHAp-(λ-Carr) hybrid materials were prepared by co-precipitation method with different content of the bio-polymer (0, 5, 10 and 20%). Synthesized materials were characterized using X-ray diffraction (XRD), Infrared spectroscopy (FT-IR), chemical analysis, Scanning Electron Microscopy (SEM), specific surface area (SS) and pHzpc measurement. The X-ray powder analysis showed that the cristallinity is affected by the presence of the biopolymer. The FT-IR spectra show the presence of $(\lambda$ -Carr) and CaHAp characteristic vibrations in the resulting product. After grafting BET measurements yielded particle specific surface areas ranging from 93 to 260 m² g⁻¹ depending on the grafted biopolymer. The adsorption capacities of methylene blue (MB) were investigated with respect to the effect of adsorbent amount, pH value, contact time, adsorbent dose, temperature and initial dye concentration. The pseudo-second-order and Freundlich isotherm equations were found to describe the adsorption mechanism. The percentage of MB removal by CaHAp and CaHAp-(\lambda-Carr)10 were equal to 81.40 % and 95.63 %, respectively. The results indicate that the modified hydroxyapatite possessed good adsorption ability towards MB dye and can be used as a low cost adsorbent for dye removal from wastewater.



The possible mode of interaction between MB dye and CallAp surface.

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Keywords: Hydroxyapatite, Biopolymer, Adsorption.

MS17-P02

Small-angle X-ray scattering studies on the self-assembly of disc shaped bicelles with DNA

Tsang-Lang Lin¹, Yuan Hu¹, Ru-Kuei Lin¹, Ching-Hsun Yang¹, Po-Wei Yang¹, U-Ser Jeng²

- Department of Engineering and System Science, National Tsing Hua University, Hsinchu, Taiwan
- National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan

email: tllin@mx.nthu.edu.tw

Disc-shaped bicelles can be formed spontaneously by mixing long-chain lipids with short-chain lipids at suitable ratios. The long-chain lipids form the bilayer core of the bicelle while the short-chain lipids form the protecting rim of the bicelle. The typical mixed lipid bicelles have a relatively uniform diameter around 20 nm. The surface charge of such bicelles can be varied by doping with cationic lipids to form cationic bicelles (CB) or with anionic lipids to form anionic bicelles (AB). Different from the typical method of encapsulating DNA with liposomes, bicelles can also be used to form cationic or anionic bicelle-DNA complexes [1-3], which can be used as nonviral vectors for improving the transfection efficiency of gene therapy. As revealed by small-angle X-ray scattering and TEM, one-dimensional alternating stacks of disc cationic bilayer plates (bicelles) and DNA arrays were formed spontaneously. DNA molecules encapsulated between the disc bilayer plates form ordered arrays with a spacing around 4~5 nm. The number of the stacking layers can be easily tuned from just a few stacks to more than one hundred stacks by adjusting the doping percentage of the cationic lipid. It is also possible to form anionic bicelle-DNA complexes with the help of the divalent cations. The DNA-ion-disk bilayer complexes are formed in the investigated range of 10 mM to 100 mM calcium ion concentrations. Other than using short-chain lipids, it was found that bicelles can also be formed at a Triton X-100 to DPPC molar ratio around 1 to 2. As compared with the diC7PC/DPPC bicelle, which can be formed for a diC7PC to DPPC molar ratio around 0.2 to 1, it seems that it takes more Triton X-100 than the short-chain lipid to form bicelles for a fixed amount of DPPC. The prepared DPPC/ Triton X-100 cationic bicelles were also found to be able to form complexes with DNA.

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Keywords: bicelle, small-angle X-ray scattering, DNA encapsulation

MS17-P03

Multi-scale characterization of bone mineral composition and structural organization

Pedro Alvarez¹, Nazaret Domínguez-Gasca², Cristina Benavides², Estefanía Sánchez-Rodríguez², Alejandro Rodríguez-Navarro²

- 1. Deparmento de Geología; Universidad de Oviedo, Oviedo, Spain
- Departamento de Mineralogia y Petrologia, Universidad de Granada, Granada, Spain

email: pedroalvarez@uniovi.es

Bone is a complex biocomposite material constituted by carbonated apatite nanocrystals deposited in an oriented fashion and integrated within an organic matrix, mostly collagen fibrils. To define how bone compositional and structural characteristics in different bone types (i.e. cortical and trabecular bone) affect relevant bone properties (i.e., mechanical properties), we have applied complementary analytical techniques such as electron microscopy, computed tomography, infrared spectroscopy and X ray diffraction. These techniques provide detailed information about the mineral and organic components of bone tissue and allow the determination of its porosity, degree of mineralization, carbonate content, mineral crystallinity and collagen cross-linking. Bone compositional parameters determined by infrared spectroscopy (e.g. degree of mineralization (PO4/Amide I), the total carbonate (CO4 1415/Amide I) are important parameters to define bone material quality and are useful to detect possible metabolic alterations associated to specific bone pathological conditions (osteoporosis, osteomalicia). BSE-SEM images of cross-section at mid-diaphysis showed notable differences in the organization of different bone types (cortical and trabecular bone) and bone structures at different scales. Analyses by means 2D X-ray diffraction showed differences between types of bone related to mineral organization and its crystallinity. The degree of alignment of the c-axis of apatite crystals can be determined from the intensity profile along Debye-Scherrer ring associated with the 002 reflection. The preferential orientation of the apatite crystals is due to an aligned arrangement of collagen fibers in cortical organization while the crystals showed randomly orientation at trabecular level. The information obtained allowed us to determine the influence of chemical composition and microstructural organization on cortical and trabecular regions in the overall bone material properties.

Keywords: bone, organization, microstructure

MS17-P04

Structural evolution of hydrated calcium oxalates

Alina Izatulina¹, Vladislav Gurzhiy¹, Maria Krzhizhanovskaya¹, Mariya Kuz'mina¹, Matteo Leoni², Olga Frank-Kamenetskaya¹

- 1. Department of Crystallography, St. Petersburg State University, St. Petersburg, Russia
- 2. University of Trento, Trento, Italy

email: alina.izatulina@mail.ru

Calcium oxalates are represented in nature by three hydrated forms: whewellite (CaC₂O₄·H₂O; COM), weddellite (CaC₂O₄·(2+*x*)H₂O; COD) and caoxite (CaC₂O₄·3H₂O; COT). Calcium oxalates are also found among the pathogenic mineral precipitates in human bone marrow, myocardium, joints, lungs, liver, thyroid gland, intestinal mucosa, eyes, and urinary system. Oxalates span therefore several fields (medicine, biology, mineralogy, materials science, etc.), which is reflected in a large number of publications. Nevertheless, many questions remain unresolved. For instance, the role of water in the formation of calcium oxalate crystal structures as well as the mechanisms of phase transition is still unclear.

Thermal stability, structural evolution pathways and phase transition mechanisms of the calcium oxalates COM, COD and COT have been analyzed using single crystal and powder X-ray diffraction techniques at non ambient conditions. The reduction of H₂O content in the structures increases dimensionality from dimers and chains to the layered structural units and from rarefied to denser sheets within the compounds whose structures are based on the 2D units. While studying the phase transitions pathways within the calcium oxalate family, two crystalline compounds have been structurally characterized for the first time (α -CaC₂O₄ and CaC₂O₄·H₂O), among which the novel COM modification has been obtained for the first time as well. The highest thermal expansion of these compounds is observed along the direction of the hydrogen bonds, whereas the lowest expansion and even contraction of the structures occur due to the displacement of neighbor layered complexes towards each other and to an orthogonalization of the monoclinic angles. Within the calcium oxalate family, whewellite should be regarded as the most stable crystalline phase at ambient conditions. Weddellite and caoxite transform to whewellite during dehydration-driven phase transition promoted by time and/or heating. Finally, we'd like to emphasize the particular importance of the structural and chemical evolution studies of calcium oxalates, as their phase transitions occur at temperatures typical of the human body and can therefore have a significant effect on health.

This work was supported by President of Russian Federation grant for leading scientific schools (no. NSh-3079.2018.5), Russian Foundation for Basic Research (no. 16-05-00986) and by the People Program (Marie Curie Actions) of the European Union's Seventh Framework Program FP7/2007-2013/ under REA grant agreement IRSES-GA-2013-610547-TAMER. The XRD measurements have been performed at the X-ray Diffraction Centre of St. Petersburg State University.

Keywords: calcium oxalate, crystal strusture, phase transition

MS17-P05

Salivary stones crystallization. Previous study

Victoria López-Acevedo¹, Álvaro Sánchez-Barrueco², Sol López-Andrés¹, José Miguel Villacampa-Aubá², Jessica Santillán-Coello², Fernando González-Galán², Gonzalo Díaz-Tapia², Carlos Cenjor-Español²

- Departamento de Mineralogía y Petrología. Facultad de Ciencias Geológicas (UCM), Madrid, Spain
- Otorhinolaryngology Service of Jiménez Diaz Foundation University Hospital, Villalba General Hospital and Infanta Elena University Hospital, Madrid, Spain

email: vcornejo@ucm.es

The present work is part of a multidisciplinary research project that is being carried out between components of the Complutense Research Group "Crystallographic and geological techniques. Non-conventional applications" and the Otorhinolaryngology Service of Jiménez Díaz Foundation University Hospital, Villalba General Hospital and Infanta Elena University Hospital from Madrid.

The sialolithiasis is a frequent cause of salivary flow obstruction that causes a pathology called chronic obstructive sialadenitis. Most salivary stones are produced in the submandibular or submaxillary gland followed by the parotid gland. Their chemical composition is carbonate and calcium phosphate, with impurities of magnesium, potassium and ammonium. The genesis of the stones is associated with the partial obstruction of a calcium-rich saliva, but to date the mechanism of their formation is not well understood [1, 2].

Through this paper we have studied salivary stones from 25 anonymous patients with different ages and gender, with different glandular and anatomical origin, most of them whole and extracted by sialoendoscopy.

The mineralogical and morphological characterization was made using XRPD, OM and SEM-EDX.

Although each of them has unique characteristics, they show a series of common features that have allowed us to suggest a crystallization model that we hope to confirm as the number of cases studied increases.

The macroscopic size of the stones ranges from 2 to 22 mm. In all of them hydroxyapatite $(Ca_{10}(OH)_2(PO_4)_6)$ and octacalcium phosphate $(Ca_8H_2(PO_4)_6, 5H_2O)$ have been identified as crystalline phases. In addition, withlockite $(Ca_3(-PO_4)_2)$ was identified in eight of the samples studied. All phases have a very low degree of crystallinity.

Morphologically, they could be defined as concentric oolites, in which an inner core stands out. The texture of the layers is granular; consisting of aggregates of microspheres whose size increases from the core, where they are nanometric, towards the surface, where they adopt botroidal appearances perceptible to the naked eye.

These morphological characteristics suggest a heterogeneous initial nucleation of multiple nuclei from organic components present in saliva. The nuclei anastomose during their growth, forming agglomerates that serve as substrate for the nucleation of new layers of spheres, repeating the process until reaching the final size. These results agree with the low degree of crystallinity observed in the diffractograms and suggest a mechanism of continuous growth, far from the equilibrium at high supersaturation, which occurs rhythmically, originating the different concentric layers in a similar way to the formation process of pearls [3].

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org/10.1083/jcb.9.2.395

Keywords: salivary stones, sialolithiasis, biocrystallization

MS17-P06

Biomineralisation of marine carbonates ion by ion growth vs. particle accretion

Wolfgang W. Schmahl¹, Erika Griesshaber¹, Xiaofei Yin¹, Martina Greiner¹, Andreas Ziegler², Paul Walther², Lourdes Fernández Diaz³, María del Mar Simonet Roda¹, Klemens Kelm⁴

- 1. Department of Earth and Environmental Sciences, Ludwig Maximilians University, Munich, Germany
- Central Facility for Electron Microscopy, University of Ulm, Ulm, Germany
- Departamento de Cristalografía y Mineralogía, Universidad Complutense de Madrid, Madrid, Spain
- 4. Institute of Materials Research, German Aerospace Center DLR, Cologne, Germany

email: wolfgang.w.schmahl@lrz.uni-muenchen.de

Ca-Carbonate teeth and skeletons of marine invertebrates show usually show a nanoparticulate morpho-topology in SEM and AFM investigations. Consequently, a paradigm evolved which explains the genesis of biominerals by accretion of carbonate-filled vesicles exocytosed by the mineralizing cells. This model of nanoparticle aggregation was supported by the proposition of "nanoparticles" or pre-nucleation clusters in carbonate solutions suggesting "non-classical" nucleation and growth of carbonates.

Since more than 10 years we studied many Ca-carbonates formed by marine organisms with AFM, SEM/EBSD, TEM and XRD. In addition, we investigated abiotic calcite growing in gels. Today, we feel that the paradigm of nanoparticle accretion as a general model for biomineralization needs to be seen with scrutiny:

i) Protein or polysaccharide gels are fibrous networks with open pores in the ~100 nm range (depending on gel concentration). The mineral forming within the gel incorporates the gel fibres and membranes and thus develops a superficial "nanoparticulate" mesocrystal-like appearance. However, the omnipresent terraces corresponding to regular crystal faces, such as {104} for calcite, indicate ion-by-ion growth of the aggregates.

ii) For most marine biocarbonates the "nanogranule-like" morphologies are in the 50-100 nm size range. The biocarbonate crystals contain incorporated organic networks with structures and size-ranges similar to the gel-grown crystals. Coccoliths are an exception: they do not contain organic matrix and show a classical crystallography. Coccoliths do grow intracellular vesicles.

iii) The "pre-nucleation clusters" in hydrous solution supposed to be responsible for "non-classical crystal growth" are an order of magnitude smaller than the "nanogranules" of biocarbonates, such that there cannot be a direct relationship.

iv) Dense aggregation of any round and similarly-sized particles leaves ~25% open pore space. In contrast, most marine biocarbonates have no such pores.

v) ACC-filled nanovesicles in epithelial cells have so far not been found, despite intensive search.

Thus, the formation of biominerals may well occur by ionby-ion growth in gel- or PILP-filled extracellular compartments, where the necessary transport of calcium and hydrogencarbonate into the compartment and of protons out of the compartment occurs by the common ion pumps and exchangers in the membranes of the epithelial cells.

Keywords: Biomineralization, Mesocrystals, EBSD

MS18- Crystallography at high pressure and dynamically compressed matter

Chairs: Dr. Damian Paliwoda, Dr. Ines Collings

MS18-P01

High-pressure single-crystal X-ray diffraction study of a model Rh complex exhibiting metallophilic interactions in the solid state

Radosław Kamiński¹, Katarzyna N. Jarzembska¹, Damian Paliwoda², Václav Petříček³, Carla Pretorius⁴, Andreas Roodt⁴

- 1. Department of Chemistry, University of Warsaw, Warsaw, Poland
- 2. Department of Chemistry, Lehigh University, Betlehem, United States of America
- Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic
- 4. Department of Chemistry and Polymer Science, Stellenbosch University, Bloemfontein, South Africa

email: rkaminski85@gmail.com

High-pressure studies of materials constitute an important field of research, as high-pressure phases often exhibit unique properties, as well as, via applying high pressure one may see what happens to a given material in real-life conditions. The detailed knowledge of materials' structure is indispensable to understand, and later to potentially sensibly control, their behaviour and function. In this respect high-pressure single-crystal X-ray diffraction experiments provide full picture of material's structure with atomic resolution.

Consequently, in this contribution we describe our recent studies of a model rhodium complex, namely LRh(CO)₂ (L = 3-benzoylacecate), which exhibits chain substructures based on the Rh...Rh interactions propagating along the Y-axis direction. It is shown the temperature does not have a significant impact on the structural parameters (except for the less obvious unit cell choice in the case of the high temperature structure). In turn, the application of high pressure leads to an interesting phase transition, in which the Rh...Rh chains differentiate noticeably. As a result the structure becomes modulated and has to be treated within a super-space approach. Thus, here the structural analysis of the new modulated phase is presented and the further prospects of using this information to explain spectroscopic behaviour under high pressure are discussed.

High-pressure experiments were conducted at the ID15B beamline of the ESRF facility (Grenoble, France) (proposal no.: CH-4903). R.K. would like to thank SONATA grant (2016/21/D/ST4/03753) from the National Science Centre in Poland for financial support. The in-house X-ray diffraction experiments were carried out at the Department of Physics, University of Warsaw, at the Rigaku Oxford Diffraction SuperNova diffractometer, which was co-financed by the European Union within the European Regional Development Fund (POIG.02.01.00-14-122/09).

Keywords: High pressure, synchrotron, rhodium complexes, modulated structures, metallophilic interactions

MS18-P02

Structural changes induced by high pressure and radiation in crystals of three cinnamic acid derivatives

Tomasz Galica¹, Julia Bąkowicz¹, Krzysztof Konieczny¹, Ilona Turowska-Tyrk¹

1. Faculty of Chemistry, Wrocław University of Science and Technology, Wrocław, Poland

email: tomasz.galica@pwr.edu.pl

The [2+2] photodimerization was conducted in crystals of 2,5-difluorocinnamic (1), 3,5-difluorocinnamic (2) and 2,6-difluorocinnamic (3) acids in ambient and high-pressure conditions. The photochemical reaction was induced stepwise by UV/vis radiation and the X-ray diffraction experiment was carried out after each step. This enabled us to monitor changes in the unit cell parameters, intermolecular geometry and product content in crystals. The influence of pressure on the direction and size of those changes was an alyzed [1].

For each compound there is a critical point below which the increasing pressure speeds up the reaction, and above which the reaction cannot be further accelerated. This is due to the changes in the geometrical parameters describing a pair of reacting molecules and the simultaneous decrease in the volume of free space.

The photochemical reactivity of three studied compounds changed in the following order: (1) > (2) > (3). To rationalize this observation we analyzed the parameters that could have an impact on the reactivity: the geometrical parameters for reacting molecules, intermolecular interactions, size and shape of free spaces in crystals and also the substituent effect. It turned out that the role of the substituent effect is important and should be considered during the studies of reactivity of cinnamic acids in crystals.

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Keywords: XRD, Photoreaction, high-pressure,

Structural behaviour of Copper(I) Iodine compounds under high pressure

Javier Gonzalez-Platas¹, Amagoia Aguirrechu-Comeron¹, Ulises R. Rodriguez-Mendoza¹, Victor Lavin¹, Sandrine Perruchas²

- 1. Departamento de Fisica. Universidad de La Laguna, La Laguna, Spain
- 2. Institut des Matériaux Jean Rouxel, Nantes, France

email: jplatas@ull.edu.es

Copper(I) iodine compounds can exhibit interesting mechanochromic and thermochromic luminecest properties with important technological applications. This fact is due two mainly factors. The first is about the large variety of structural configurations as staircase ladders linked by briding N-donor ligands or cubane clusters with phospine ligand [1-2] among others. The second is the behaviour of these compounds under external stimuli inducing structural changes on bond distances, dihedral and/or torsional angles and packing between molecules. There are a lot of studies where this external stimuli is the temperature and how it affect the interactions of Cu., Cu. Other similar studies are based on mechanical stimuli as grinding but only a few are using the pressure. We are reporting the structural and luminescence studies under high pressure, at room temperature under high pressure, of three copper iodine samples with different configuration. A cubane cluster type Cu4I4 (PPh2(CH2=CH2), 1D coordination polymer (staircase) CuI(6-methylquinoline) and 2D coordination polymer (staircase). For such compounds we present an analysis about their compressibility and bulk modulus through isothermal Equation of State calculations [3]



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Keywords: Copper(I), Pressure, EoS

High-pressure neutron measurements of the highly-polymorphic 'ROY'

Nicholas Funnell¹, Craig Bull¹, Christopher Ridley¹, Silvia Capelli¹

1. UKRI - ISIS Neutron and Muon Facility, Didcot, United Kingdom

email: nick.funnell@stfc.ac.uk

Where neutron-powder measurements are needed to discriminate between similar-Z elements, identify magnetic behaviour, or simply locate hydrogen atoms, large sample volumes are generally required for a successful measurement. This might appear problematic for high-pressure experiments where small sample volumes are necessary to access higher pressures. However, the large-volume Paris-Edinburgh press on the high-pressure PEARL beamline at ISIS, UK, allows us to make such measurements—striking a balance between sample quantity and accessible pressure.[1]

5-methyl-2-[(2-nitrophenyl)amino]-3-thiophenecarbonitrile is one of the most polymorphic organic materials known in the Cambridge Structural Database. It is more colloquially known as 'ROY', owing to the red, orange, and yellow polymorphs that it forms, all occurring under ambient conditions.[2] In this presentation, a recent compression study on ROY and its behaviour up to 9.3 GPa will be reported. [3] We show that the quality of PEARL data obtained, and careful DFT-assisted guidance of the refinement procedure, produce usable structural models from a weakly-scattering, hydrogenated sample. We discuss its structural response in the context of lattice- and intermolecular-energy calculations.

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Keywords: pressure, neutron, polymorphism

MS18-P05

A crystallographic study of L-threonine to extremely high pressures

Nico Giordano¹, Simon Parsons¹, Christine Beavers², Simon Teat²

- School of Chemistry and Centre for Science at Extreme Conditions, The University of Edinburgh, Edinburgh, United Kingdom
- 2. Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, United States of America

email: nico.giordano@hotmail.co.uk

Our work focuses on pushing the boundaries of high-pressure crystallography on soft molecular systems. We have successfully determined crystal structures of the essential amino acid, L-threonine ($C_4H_9NO_3$) to 22 GPa.

L-threonine is zwitterionic in the solid-state, comprising of an ammonium cation and a carboxylate anion. Each molecule is connected by four H-bonds, resulting in a $P 2_1 2_1 2_1$ (Z=4) crystal structure with zig-zag chains formed along the long crystallographic axis, linked by carboxylate and hydroxyl interactions. Adjacent chains are interconnected by off-axis H-bonds between nitrile and carboxylate groups to form pleated layers. Single-crystal X-ray diffraction experiments were performed with synchrotron radiation in series using the diamond anvil cell and neon pressure transmitting medium. A reversible pressure induced phase transition going from the $P 2_1 2_1 2_1 (Z'=1)$ crystal structure to $P 2_1 (Z'=2)$ was observed at 18 GPa. All H-bonds shorten resulting in conformational changes of the carboxylate, hydroxyl and methyl moieties. Structure refinements were validated against periodic-DFT (CASTEP) optimisations and prior works.^[1] Crystal lattice energies and the most energetically significant H-bond interactions for all structures were examined by the PIXEL method.[2]

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Keywords: amino acid, hydrogen-bond

1-Dimensional *sp*³-carbon nanostructures synthesized through nanocasting at high pressure

Damian Paliwoda¹, Maria Baldini², Venkata S. Bhadram², Shah Najiba¹, Timothy A. Strobel², Kai Landskron¹

- Department of Chemistry, Lehigh University, Bethlehem, PA, United States of America
- Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC, United States of America

email: dap216@lehigh.edu

One-dimensional diamond mesostructures (1D-diamond) are of interest as heat-conducting wires, and as mechanically reinforcing material in diamond/polymer composites because of the superlative mechanical strength and thermal conductivity of diamond. Thus far, 1D-diamond has been produced by CVD methods.1 However, CVD methods do not allow for the economic production of bulk quantities of 1D-diamond, and it is difficult to control the diameters and length of the produced 1D-diamond structures. Currently there is no high-pressure synthesis available for the bulk synthesis of one-dimensional diamond mesostructures. The basic problem is that at high-pressure conditions it is difficult to direct the growth of diamond crystals in a specific direction. In addition, any one-dimensional structure formed can easily aggregate with another which prevents any further processing after the high-pressure synthesis.²

Herein, we present the synthesis of diamond-like 1D sp^3 -carbon mesostructures from benzene inside the 1-dimensional channels of periodic mesoporous silica SBA-15 at pressures above 20 GPa and room temperature (Figure 1). Inside the silica template, the 1D- sp^3 -carbon nanostructures are spatially separated from each other preventing their aggregation at the high-pressure conditions. Small Angle and X-Ray Scattering data collected for SBA-15/benzene composite clearly shows that silica mesostructure retains its periodic order upon compression, while X-ray diffraction experiments allow to track pressure-induced structural transformations of benzene.

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Keywords: one-dimensional nanomaterials, high pressure, diamond anvil cell

MS18-P07

Integrated solutions for most efficient in house high-pressure single crystal experiments

Martin Adam¹, Przemyslaw Dera², Michael Ruf³

- 1. Bruker AXS GmbH, Karlsruhe, Germany
- 2. University of Hawaii at Manoa, Honolulu, United States of America
- 3, Bruker AXS Inc., Madison, United States of America

email: martin.adam@bruker.com

Within the last decade high pressure studies have received significant increase of interest. Present typical applications range from the investigation of solid-state organics as part of the pharmaceutical drug development to the study of rocks and minerals with applied pressures of up to 50 GPa. While in the past it has been almost impossible to accommodate and extend standard in-house solutions, i.e. hardware and software, to the needs of high-pressure crystallography, today this picture has changed completely. Modern high-performance software, such as APEX3, has been developed to address the intrinsic challenges of high pressure crystallography, particularly with respect to sample alignment, indexing, data integration and scaling. This complements the significantly higher flexibility available in the hardware setup. Current instrumentation can easily be used for routine low temperature data collections, fully optimized with respect to minimizing air scattering and achieving full completeness and desired data multiplicity. Within just a few minutes the same instrument can be converted into an optimized solution for high pressure data collection, e.g. for the investigation of organic solid state material in a diamond anvil cell (DAC). Electronic component recognition ensures automated reconfiguration and validation of the instrument. This approach avoids invalid and useless configurations on the one hand, while on the other hand taking the special requirements of a high-pressure experiment into account. For example, even with the limitations implied by the DAC best possible, completeness and data redundancy is automatically ensured.

Using a D8 VENTURE with a fixed-chi stage we will demonstrate the advanced hardware capabilities and processing methods based on the monoclinic polymorph of the sulfonium ylid. The high flexibility of the D8 VENTURE design will be further demonstrated in the second part of the presentation: For the investigation of miniscule mineral crystals enclosed in diamond anvil cells, functionality typically only available at synchrotron facilities has been added to the in-house system. These features include highly accurate, motorized sample positioning and the ability to monitor intensity of the X-ray beam passing through diamond anvil cell. The latter is used both for DAC alignment, as well as for correcting measured intensity data. The availability of online pressure measurements based on ruby fluorescence completes the extension of the D8 VENTURE, making the system "a little synchrotron at home".

Lab-based experiments up to 50 GPa with synchrotron-sized high-pressure single-crystal samples of even triclinic symmetry will be presented.



Keywords: in-house solution, synchrotron, automation

MS18-P08

1-Hydroxypyrene under pressure - crystal morphology affected by hydrogen bond

Roman Gajda1, Maura Malińska1, Anna Maka1

1. Department of Chemistry, University of Warsaw, Warsaw, Poland

email: romanbg@chem.uw.edu.pl

We have investigated single crystals of 1-hydroxypyrene. This is a relatively uncomplicated crystal structure, where monoclinic unit cell consists of four molecules, kept together by O-H...O hydrogen bonds and π -stacking intermolecular interactions. These interactions, as well as characteristic features of 1-hydroxypyrene molecules, such as conjugated aromatic rings, strongly affect the crystal morphology.

It is already known, that the morphology of a particular crystal can be assessed with the use of the attachment energy model [1]. There are also papers describing influence of solvent environment on crystal morphology [2,3].

In the case of 1-hydroxypyrene, when single crystals are grown from non-polar solvents such as n-pentane or n-hexane, they crystallize in form of long, thin needles. Calculations of the attachment energy confirm this morphology. However, when single crystals of 1-hydroxypyrene are grown from polar solvents such as methanol or acetone, they crystallize in form of plates.

What is more, we have also performed crystallization of 1-hydroxypyrene under pressure, with the use of Diamond-Anvil Cell (DAC). Surprisingly, this experiment has revealed that under pressure, even where polar solvent was used, 1-hydroxypyrene again crystallizes in the form of needles, which are extremely flexible. Crystals are so pliable that during crystal-growth they can easily bend, even about almost 90 degree, rather than grow thicker. This behavior of crystals in DAC reveals dominant influence of hydrogen bonds on morphology of the crystal, and suggests, that the role of the solvent's polarity in crystallization process diminishes with pressure. Molecules of 1-hydroxypyrene form substructures which are kept together by above-mentioned hydrogen bonds. Such substructures resemble columns where aromatic rings of neighbouring molecules form π -stacks, thus enhancing the effects of H-bonding. These columns coincide with the long direction of the needle and allow it for the crystal's flexibility. It can also explain negligible compressibility with pressure in that particular direction in the crystal lattice.

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Keywords: high pressure, hydrogen bond, crystal morphology

High pressure pair distribution function study of amorphous silica in helium

Jerome Rouquette¹, Julien Haines¹, Daniel Bowron², David Keen², Mathieu Kint³, Coralie Weigel³

- ICGM, UMR CNRS 5253, Université de Montpellier. CC01504, 34095 Montpellier, Montpellier, Fraance, France
- ISIS, Rutherford Appleton Laboratory, Harwell Oxford, Didcot, OX11 0QX, UK, Didcot, OX11 0QX, United Kingdom
- L2C, UMR CNRS 5221, Université de Montpellier. CC069, 34095 Montpellier, Montpellier, France

email: jerome.rouquette@umontpellier.fr

Glasses are used for a large number of technological and everyday applications. Among them, the system that has been most widely investigated is amorphous silica (a-SiO₂). The structure of aSiO₂ consists of corner-sharing SiO₄ tetrahedra which form *n*-fold rings (with $n \ge 2$, in a-SiO₂ mostly n = 4, 5, 6, 7, 8). The absence of Bragg reflections in diffraction experiments precludes the use of traditional crystallographic techniques to determine their atomic structure. However, it is clear that these materials possess well-defined local structure on the nanometer scale, which is often linked with their physical properties. Local structure can be obtained using x-ray total scattering from which the distribution of interatomic separations can be measured via the pair distribution function (PDF). High-quality PDFs require high-energy photons and access to large scattering angles to measure data to high values of momentum transfer (Q = $4\pi \sin \theta$ θ/λ).

It was recently discovered that when helium or argon are used as pressure transmitting medium, a-SiO₂ exhibits a completely distinct compression behavior[1]. The compressibility of a-SiO₂ drastically decreases in a helium medium which can easily be understood by the penetration of helium atoms ($r_{\rm He}$ =1.3 Å) in *n*-fold rings (with $n \ge 6$, $r_{6.60d}$ ring =1.5 Å) which prevents collapse of the rings, contrary to argon ($r_{\rm Ar}$ =1.88 Å), and therefore the densification of the material; based on a poromechanics model [2], up to 0.53 mole He can be incorporated under pressure. In order to determine the structural change dependence of helium adsorption on a-SiO₂, high pressure PDF measurements were undertaken.

High-pressure high-quality data were obtained using 61 Kev photons up to 22 Å⁻¹. The total scattering data was refined by the reverse Monte Carlo (RMC) method [3] in order to obtain changes to bond-angle distributions and network topology of a-SiO₂ in helium as a function of pressure. Partial PDFs were obtained and permitted to understand the structural modifications induced by the helium adsorption at high pressure which consist in: i) a broadening of the Si-Si bond distribution(inter-tetrahedra distances) in the first and second coordination shells; as a consequence appearance of a new contribution is also observed above 3 Å for the Si-O PDF, ii) a decrease in the O-He distance distribution with increasing pressure which becomes more ordered as a result of helium confinement. References:

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Keywords: PDF study, amorphous silica, helium asorption

Crystal structure and spectroscopic properties of 1-(pyren-1-yl)but-2-yn-1-one under pressure

Anna Makal¹, Joanna Krzeszczakowska¹

1. Biological and Chemical Research Centre, Chemistry Department, Warsaw, Poland

email: amakal@chem.uw.edu.pl

Controlling properties of materials, such as fluorescence, by subjecting them to macroscopic external physical stimuli (temperature, high-pressure, electric field ...) is a challenge for basic research and an important issue for developing industrial applications. Understanding the mechanisms governing the changes resulting from external stimuli is an essential step in the design of new materials and in optimizing their properties.

Pyrene and its derivatives constitute one of the best studied groups of organic fluorophores[1] characterized by relatively long-lived fluorescence (ns – µs excited-state lifetimes), high quantum yields and high environment sensitivity. Multi-substituted pyrene derivatives have already found applications in pressure sensors[2].

One particular property of these fluorophores is their propensity to form excimers. Another is their enhanced solid-state fluorescence. Molecular ordering, resulting from π ... π -stacking in the crystal lattice, seems to augment this process. The phenomenon can be considered peculiar, given that clustering of molecules is often raised as the reason for fluorescence quenching in other materials. In light of existing[3] and potential applications of pyrene derivatives in photo-cells and LEDs, a detailed study of the phenomena responsible for efficient fluorescence in solid state seems pertinent. Application of high pressure to the flat, aromatic pyrene derivatives in the crystal lattice should result in forced, closer placement of the aromatic fragments and may be considered as an experimental model for excimer formation, strictly controlled by the applied pressure.

Here we present the results of structural and spectroscopic investigation of a model, simple, monosubstituted pyrene derivative, which in solid state shows 6-fold increase in the quantum efficiency of fluorescence when compared with solution. The crystal structure is based on infinite face-to-face π -stacks of molecules.

Structural analysis at several pressures confirmed minute changes within molecular structure, accompanied by significant modifications of the intermolecular interactions: it was possible to decrease the distance between the flat pyrene moieties by over 0.2Å. These changes were consistent with the changes predicted by means of quantum-mechanical calculations, performed in periodic conditions. The decrease in intermolecular distance can be directly correlated with the decrease of the gap between the valence and conduction bands, marking the compound as an indirect semi-conductor. The changes in the electronic structure find confirmation in the sample's color change under pressure and the spectacular batochromic shift of the fluorescence maximum by 100nm between the atmospheric pressure and 3GPa. References:

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Keywords: poly-aromatic hydrocarbons, piezochromism, UV-VIS fluorescence

Studying weak interactions in crystals at high pressures: when hardware matters

Marcus Mueller¹, Boris A. Zakharov², Zoltan Gal³, Dyanne Cruickshank³, Elena V. Boldyreva³

- 1. DECTRIS Ltd, Baden-Daettwil, Switzerland
- 2. Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia
- 3. Rigaku Oxford Diffraction, Chalgrove, United Kingdom

email: marcus.mueller@dectris.com

Obtaining reliable information on intermolecular interactions in crystal structures relies on highest-quality diffraction data. This is even more the case when collecting high-pressure data from a sample in a diamond anvil cell (DAC) that limits completeness and observable reciprocal space. For such challenges, hardware becomes a crucial factor. A new generation of laboratory diffractometers using advanced sources and Hybrid Photon Counting (HPC) detectors has been developed, enabling the collection of data at high pressures from even small and weakly diffracting crystals. However, high-quality data alone does not guarantee a high-quality structural model and careful processing is critical for data collected from a sample in a DAC.

We will present a comparison of the results obtained with a previous generation laboratory diffractometer and the latest generation, using a PhotonJet-S microfocus source with silver radiation and a PILATUS3 R CdTe 300K HPC detector. Our results show that the latest generation hardware allows for substantially shorter measurement times, higher data quality, and refinement results not possible with the previous generation. Furthermore, we will discuss the impact of different data processing strategies on the results of crystal structure refinement.

MS18-P12

Role of size and electronegativity of the transition metal ion, on the high pressure behavior of dimethyl ammonium metal formates

Abhishek Chitnis¹, Mirosław Maczka², Himal Bhatt¹, Mukund Deo¹, Nandini Garg¹

- 1. Bhabha Atomic Research Centre, Mumbai, India
- 2. Institute of low temperature and structure research, Polish academy of Sciences, Poland, Wrocław, Poland

email: abhishekchitnis87@gmail.com

Dimethyl ammonium metal formates (DmAMF) are important metal organic framework compounds (MOF). Though, they have been extensively studied at low temperature, to perceive their ferroelectric transition due to H-bonding [1], thermal expansion properties, stress-strain dependence, magneto-electric tunability [2] etc., very few studies have been carried out on these materials at high pressure. As per our studies, application of pressure deforms the formate network. This results in the distortion of the cubo-octahedral cavities formed by it, leading to the structural phase transition [3]. However, the role, of size and electronegativity of the transition metal ion, on this phase transition, has not been addressed so far.

We have studied the dependency of divalent metal ion on pressure evolution of DmAMF (M = Ni, Co, Mn, Cd). Our IR spectroscopic studies show that the framework structure of the formates with transition metal cations having smaller ionic radii $[Ni^{2+}(0.69A^{\circ}) < Co^{2+}(0.745A^{\circ}) < Mn^{2+}(0.83A^{\circ})$ < Cd²⁺(0.95A°)] distort at higher pressures and the degree of distortion is less than the formates with higher cationic radii. It was also observed that the lower flexibility of the formate network in these compounds can be attributed to the stronger metal-formate coordination bond. In addition, on application of pressure the CNC mode softens [Fig (c) & (d)] and some of the hydrogen bonds weaken [Fig (a) & (b)] in the formates having smaller ionic radii cations, indicating that the electronegativity of the metal ion plays a vital role in the high pressure behavior of the coordination and hydrogen bonds. This information can help us to design new MOF's with tailored properties. Further results will be discussed.



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Keywords: MOF, High pressure, IR

MS19- Materials on energy saving and climate sustainability

Chairs: Dr. Klaudia Hradil, Dr. Claudia Weidenthaler

MS19-P01

Metal hydro-borates for Li- and Na-ion batteries

Radovan Černý¹, Emilie Didelot¹, Yolanda Sadikin¹, Matteo Brighi¹, Fabrizio Murgia¹

1. Laboratory of Crystallography, DQMP, University of Geneva, Geneva, Switzerland

email: radovan.cerny@unige.ch

Complex hydrides based on light hydro-borate anions such as borohydride BH₁⁻ or *closo*-borate anion B₁₂H₁₂⁻⁻ find their place as solid stores for hydrogen, and since recently, also as solid electrolytes in Li- and Na-ion batteries. The mobility of the cations depends on the pathways available in the anion packing, chemical interaction of cations with anions and on the anion thermal motion such as tumbling or rotation. While the latter two require important experimental and theoretical effort, the first parameter can be easily analysed and quantified from the crystal structure data obtained by X-ray diffraction. A thorough crystal chemistry analysis of observed crystal structures, allows us to find the structural aristotypes and to draw conclusions about the bonding and building principles in this important category of materials as it was done recently for the borohydrides (Figure 1).

Among others, the modification of Na₂B₁₂H₁₂, promising Na-ion solid electrolyte, by anion modification and anion mixing will be shown.¹⁻² Novel synthetic way completed by *ab inito* structural characterization using synchrotron X-ray powder diffraction and *ab initio* calculation allowed discovery of several 3*d* transition metal *closo*-borates - potentially battery electrodes (Figure 2).³



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 Sadikin Y., Didelot E., Łodziana Z., Černý R., submitted to Dalton Trans.

Keywords: Na-ion battery, borate, transition metal

MS19-P02

Solvent-free synthesis of heterometallic metal-organic frameworks for the electrocatalytic reduction of carbon dioxide

Maite Perfecto Irigaray¹, Jonathan Albo², Garikoitz Beobide¹, Oscar Castillo¹, Angel Irabien², Sonia Pérez-Yáñez¹

- 1. Department of Inorganic Chemistry, University of the Basque Country (UPV/EHU)., Leioa (Bizkaia), Spain
- 2. Department of Chemical & Biomolecular Engineering, University of Cantabria (UC), Santander, Spain

email: maite.perfecto2@gmail.com

Herein we report the solvent-free synthesis and doping of the benchmark HKUST-1(Cu) as a facile route to afford heterometallic MOFs and their proficient behaviour as electrocatalytic materials in the carbon dioxide reduction to alcohols. Precisely, Zn(II), Ru(III) and Pd(II) were selected as doping metals (M_D) with the aim of partially replacing the Cu(II) atoms of the pristine structure to afford HKUST-1(Cu,M_D) type materials.

The introduction of a doping element implies a slight increase of the cell parameter with respect to the homometallic HKUST-1. This fact is attributable to the occurrence of longer M \cdots O_{carboxylate} coordination bond distances that implies the presence of the dopant in the paddle-wheel shaped dinuclear [M₂(OOC)₄] secondary building unit. In the case of Ru(1II) and Pd(II), which are elements of the second transition series, their greater ionic radii values are consistent with an increase in coordination bond distances and cell parameters. On the contrary, Zn(II) exhibits a rather similar ionic radius to that of Cu(II), but the Jahn-Teller effect of Cu(II) (d⁹) implies shorter equatorial coordination distances than those found in analogous paddle-wheel shaped Zn(II) complexes.¹

Prepared samples were processed as gas diffusion electrodes (GDEs) and assembled in a continuous flow filter-press electrochemical cell with the aim of converting CO_2 into added-value chemicals.² The obtained products are mainly methanol and ethanol with Faradaic efficiencies that range from 6 to 60%, which are values comparable or greater than those provided by conventionally used elemental copper and copper oxides.



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Keywords: Heterometallic MOFs, solvent-free synthesis, CO_2 reduction.

MS19-P03

Two polymorphs of a fibrous titanium oxophosphate as repository for active metal cations

Santiago Garcia-Granda¹

 Department of Physical and Analytical Chemistry, University of Oviedo-CINN., Oviedo - 33006, Spain

email: sgg@uniovi.es

The pioneering studies on crystalline titanium phosphates were conducted by the Alberti Lab in the University of Perugia (Italy) and emerged in the wake of the work of the Clearfield Lab (USA) on zirconium phosphates, not to mention the contributions from the Soviet school, especially the Chernukov Lab in Nizhni Nóvgorod (Russia). In this context, our group at the University of Oviedo (Spain) published its first articles on this topic at the beginning of the 1980s. In the last decades, a great variety of metal phosphates has been synthesized and characterized. These compounds exhibit a multitude of fascinating structures and the dimensionality of their inorganic framework encompasses one-dimensional chain or ladder structures, two-dimensional layers and three-dimensional structures possessing channels of different sizes [1]. Two Ti₂O(PO₄)₂·2H₂O 3D-polymorphs (r-TiP and π -TiP) were prepared hydrothermally [2], and the crystal structure of two polymorphs were solved ab initio from synchrotron X-ray powder diffraction data. The topology of two fibrous materials consists of a Ti/P/O framework enclosing two different linear channels parallel to the direction of fibers growth, both containing water molecules coordinated to only one of two octahedral-coordinated independent titanium atoms. Since the synthesis of r-TiP and π -TiP, and although this compound has been the subject of much attention and studies, our renewed interest in this material broke out as a result of its measurable thermally activated nitrogen-adsorption [3]. This behavior constitutes the first example of nitrogen-fixation by an inorganic material at above-ambient temperature. Despite of their neutral network, these compounds exhibit a surprising ability for the intra-crystalline incorporation of metal cations into their structural channels maintaining its fibrous topology. Here, we report the synthesis and characterization of metal-based materials with potential use as photoluminescent devices (europium), bioactive systems (silver), or anodes for metal-ion batteries (alkali metals).

Acknowledgments. This work was financially supported by Spanish MINECO (MAT2016-78155-C2-1-R).

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Keywords: Titanium-phosphate, photoluminescence, metal-ionbatteries.

MS19-P04

Structural, dielectric and photoelectrochemical properties of new lead-free ceramics of composition Ba_{0.925}Bi_{0.05}(Ti_{0.95-x}Zr_x)Sn_{0.05}O₃

Kamel Taïbi¹, Nesrine Taïbi-Haddadou¹, Abdelilah Lahmar², Gharib Rekhila³, Mohamed Trari³

- 1. Crystallography and Thermodynamics Laboratory, Faculty of Chemistry USTHB, Algiers, Algeria
- 2. Physical Laboratory of Condensed Matter, Picardie University, Amiens, France
- 3. Laboratory of Storage and Valorization of Renewable Energies, Faculty of Chemistry USTHB, Algiers, Algeria

email: kameltaibi.dz@gmail.com

Classical ferroelectrics and relaxors are two distinct classes of materials [1]. Among these, BaTiO3 is the best-known prototype of classical ferroelectric materials characterized by three phase transitions: rhombohedral-orthorhombic-tetragonal-cubic. The ferroelectric (tetragonal) -paraelectric (cubic) phase transition occurs at 120 °C and the orthorhombic-tetragonal transition occurs at low temperature (~ 5 °C). The improvement of the properties of BaTiO3 has been the subject of considerable efforts for several years. The abundant literature has shown that many substitutions have been tried in (Ti and/or Ba) sites. Some of these substitutions give rise to a particular dielectric behavior known as relaxor. In addition to the usual applications of ferroelectric materials, relaxors are used in the fabrication of dielectrics for capacitors and actuators [2]. Unfortunately, these materials are based on lead which is harmful to the environment. As a result, research is directed towards environmentally friendly applications using leadfree materials as alternatives. It is in this context that the present study was conducted. We have initially elaborated new ceramics of formula Ba0.925Bi0.05 (Ti0.95-xZrx) Sn0.05O3 and symbolized by the term BBiTZxS (x = 0.05, 0.15, 0.20; 25, 0.30). After that, we studied the evolution of the structure and the dielectric properties as a function of Zr composition. The characterizations were performed by X-ray Diffraction, Raman Spectroscopy and dielectric measurements as a function of temperature. The results show a classical ferroelectric behavior at low concentrations of Zr which turns into a relaxor when the Zr content increases. On the other hand, preliminary photoelectrochemical investigations showed appropriate position of the energetic band of these materials which is very interest for photocatalysis applications while respecting the environment.

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Keywords: Lead-free, Ferroelectric relaxor, Photoelectrochemical

MS19-P05

Local structure of the supported Keggin and Wells-Dawson heteropolyacids and its consequence on their (photo)catalytic activity

Giuseppe Marci¹, Elisa García-López¹, Leonardo Palmisano¹, Igor Krivtsov², Aida Serrano³

- 1. Department of Energy, Information Engineering and Mathematical Models (DEIM), University of Palermo, Palermo, Italy
- Chemical and Environmental Engineering, University of Oviedo, Oviedo, Spain
- Spanish CRG BM25 SpLine Beamline at the ESRF, Grenoble, France

email: giuseppe.marci@unipa.it

Keggin and Wells-Dawson heteropolyanions, $PW_{12}O_{40}^{-5}$ and $P_2W_{18}O_{62}^{-6}$, respectively, are nanosized transition metal-oxygen clusters belonging to the heteropolyacids (HPAs) family. They are widely used as catalysts, due to their strong Brönsted acidity, and their dispersion on solid supports favours the accessibility to their acid sites increasing their catalytic activity. Notably, the UV-irradiation significantly increases their catalytic performance [1].

A series of binary materials composed of Keggin or Wells-Dawson HPAs and SiO2, TiO2, ZrO2 or C3N4 has been prepared by impregnation and/or solvothermal methods. Remarkable differences in the (photo)catalytic activities of unsupported HPAs and binary materials are related to the structural changes of the supported HPAs due to the cluster-support interaction, which modifies their acidic strength and redox potentials. The nature of the support, particularly its acidic or basic character, defines the state of the deposited HPA. The application of XAS allowed to study the modes of interaction between the metal-oxide cluster and the support surface. Fitting of W L3-edge EXAFS spectrum of the HPA/SiO₂ prepared by impregnation revealed only a slight increment of the coordination number of the tungsten atom both in W=O and W-O-W bonds, suggesting that the supported HPA remained almost intact. The solvothermal impregnation, although gave almost the same result for silica support, drastically affected the W arrangement in HPA/ TiO₂ and HPA/ZrO₂. The increase of the coordination number of W=O and the decrease of that of the W-O-W implies the occurrence of strong HPA interactions with the TiO₂ and ZrO₂ surfaces. For the solvothermal preparation of the HPA-oxide composites the increase of the W=O coordination number followed the sequence SiO₂<TiO₂<ZrO₂ having the values of 1.25, 3.80, 4.40, respectively. This dramatic change could be explained by the partial destruction of the HPA cluster forming WO₃ species. These changes, in addition to the bulk and surface features of the supported HPAs, influenced the reaction performance of the (photo)catalytic propylene hydration [3] and 2-propanol dehydration [4,5] to a significant extent.

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Keywords: heteropolyacid, polyoxometalate, Keggin, Wells-Dawson, structure-reactivity influence, catalysis, photocatalysis, XAS, XANES, EXAFS
Metalloporphyrinic solid frameworks: catalytic activity

M. Karmele Urtiaga¹, Arkaitz Fidalgo¹, Eder Amayuelas¹, Begoña Bazán², Gotzone Barandika^{2,3}, María Isabel Arriortua^{1,2}

- Mineralogy and Petrology Department, University of the Basque Country (UPV/EHU), Barrio Sarriena s/n, 48940 Leioa, Spain
- BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, Barrio Sarriena s/n, 48940 Leioa, Spain
- Inorganic Chamistry Department, University of the Basque Country (UPV/EHU), Barrio Sarriena s/n, 48940 Leioa, Spain

email: karmele.urtiaga@ehu.eus

Porphyrin molecules are excellent candidates for bridging ligands in building solid networks because of their rigidity, large physical dimensions, tunable peripheral substituents, and an additional metallation site in the core of the fully conjugated macrocyclic compound. Thus, metalloporphyrin complexes play an important role in natural systems, carrying out essential functions in photosynthesis, oxygen transport, electron carrier and catalytic reactions. These functions are especially interesting if reproduced in the solid state. In fact, metalloporphyrinic solid networks can be extended in the three dimensions of the space through covalent and hydrogen bonds as well as through π interactions. As a result, robust, thermally stable, solid coordination frameworks SCFs can be produced.1 Porous coordination frameworks are called MOFs (metal-organic frameworks),2 and their stability is one of their weakest points, so the reticular chemistry of MOFs can be used to produce stable networks based on metalloporphyrins.3 When porous networks are produced, applications like gas adsorption and heterogeneous catalysis are available.

In this context, our research group has a large experience in the synthesis and characterization of porphyrin-based SCFs, with different peripheral substituents such as carboxilates and sulfonates: meso-tetra(4-phenyl)porphyrin (TPP), the meso-tetra(4-carboxyphenyl)porphyrin (TCPP), and the meso-tetraphenyl porphine-tetrasulfonate (TPPS). The work herein presented is focused on the catalytic activity of a family of porphyrinic solid frameworks. The as-produced SCFs have been exhaustively characterized. The catalytic activity has been investigated for some reactions: oxidation of alcohols, aldol and Knoevenagel condensations and onepot cascade reaction for the acetal hydrolysis, followed by a C-C Knoevenagel condensation. In most of the studies compounds, this activity, as heterogeneous catalyst, shows high conversion and TOF (turnover frequencies) values.

Acknowledgements

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Keywords: Metalloporphyrin, MOF, catalysis

Environmental-friendly materials by alkali activation

Serena Chiara Tarantino¹, Roberta Occhipinti¹, Gennaro Ventruti¹, Michele Zema¹

 Department of Earth and Environmental Sciences, University of Pavia, Pavia, Italy

email: serenachiara.tarantino@unipv.it

Alkali activation is the chemical process through which an aluminosilicate powder (referred to as the precursor) interact with a strongly alkaline medium (the activator) to yield ceramic-like materials with good binding properties. The process occurs at room temperature starting from waste or industrial by-products, allowing for a significant reduction of emissions of greenhouse gases. Nowadays, Alkali Activated Materials (AAMs) have emerged as novel engineering materials with potential use in many application fields, in particular as environmental-friendly alternative to traditional construction materials. AAMs exhibit properties, which include formability comparable to epoxies, high temperature stability, chemical resistance comparable to ceramic oxides and compressive strength superior to concrete. Moreover, they show adsorptive properties towards metal cations, wastewater pollutants and CO2. Tailoring the properties of AAMs for specific applications requires full control on synthesis conditions and understanding of the structural and microstructural features of the final product.

In a recent work from our group, the feasibility of using sulphate-bearing kaolin for alkali activation has been assessed [1]. Alunite, KAl₃(SO₄)₂(OH)₆, which is present in the kaolin, hinders the use of these clays in the ceramic industry due to the release of SO_x at HT. Nonetheless, it is a potential source of potassium and aluminium. AAMs obtained at temperature below desulphation show high thermal stability and compressive strength as high as ca. 80 MPa. Thenardite, Na₂SO₄, deriving from the dissolution of alunite, was observed in the final products. Nonetheless, sulphate is still present in the samples after leaching. In order to identify the possible non-soluble sulphate-bearing phases and evaluate the possibility of sulphate uptake by the gel itself, zeolitisation of kaolin was carried out under molten conditions [2] in the absence or presence of sulphate.

Kaolin-alunite mixtures were melted with NaOH at 550°C, incubated in vessels with distilled water, and resulting powders characterized by Rietveld refinements of XRPD patterns, FT-IR and SEM-EDS. Zeolites Y and A crystallize in sulphate-free mixtures, as expected, while sulphate-bearing CAN is the main reaction product of all alunite-containing batches. Therefore, sulphate ion could drive the nucleation and precipitation of CAN-type zeolites at room pressure, analogously to CO_3^- , NO_3^- , and SO_3^{-2} [3]. These findings suggest that sulphate may have the same effect also in alkali activation process. This hypothesis is supported by preliminary ²⁹Si and ²⁷Al NMR data, indicating cancrinite as one of the candidate phases for trapping sulphur in AAMs.

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Keywords: Alkali Activated Materials, framework silicate, zeolite

Influence of the glass-ceramic synthesis route on the ionicconductivity of the sodium solid electrolyte Na₂O-Y₂O₃-SiO₂ (NYS)

Wolfram Münchgesang¹, Dörthe Wagner², Mykhaylo Motylenko³, Jochen Schilm², David Rafaja³, Dirk C. Meyer¹

- 1. Institute of Experimental Physics TU Bergakademie Freiberg, Freiberg, Germany
- Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Dresden, Germany
- Institute of Materials Science Structure Research TU Bergakademie Freiberg, Freiberg, Germany

email: wolfram.muenchgesang@physik.tu-freiberg.de

The development of room temperature solid electrolytes (SEs) is one of the keys for the realization of solid-state batteries – a post lithiumion technology, with probably better performance than this. For such a SE, a glass-ceramic synthesis route (GCSR) is particularly suitable, because this is less expensive than other production methods and can be used on an industrial scale. The maximum achievable conductivy (C) of SEs is determined by the used ionic-conductive phase (ICP), in our case this is the crystalline phase Na₃YS1₄O₁₂. The practical C is decisively influenced by the microstructure of the SE, in particular the realization of a suitable percolation path; which is determined by the proportion of the ICP and their crosslinking. We will present the influence of different GCSR on the microstructure of the SE and the resulting conductivity change.

Keywords: sodium solid electrolyte, glass-ceramic synthesis, ionic conductivity

MS19-P09

New insight in the CO₂ photo-activation mechanism in artificial photosynthesis

Víctor Antonio de la Peña O'Shea¹, Fernando Fresno¹, Ignacio Villar¹, Mariam Barawi¹, Patricia Reñones¹, Elena Alfonso¹, Alba García-Sánchez¹, Marta Liras¹, Raúl Pérez¹

1. Photoactivated Processes Unit, IMDEA Energy Institute, Móstoles, Spain

email: victor.delapenya@imdea.org

An interesting route for the valorization of CO_2 consists on its photocatalytic conversion into fuels and/or chemicals in the presence of water and suited photocatalyst [1]; this process is also known as Artificial Photosynthesis (AP). Such conversion is a quite challenging process since CO_2 is a very stable compound and its reduction involves a series of multi-electron reactions. Extensive efforts are focused on improving the photocatalytic efficiencies, especially when using water as the electron donor. Generally, this process suffers from very low quantum yields and non-selective product distributions, due to the complexity of the involved multi-step reactions.

During the last years, a series of innovative materials with versatile properties and multifunctional character, known as hybrid materials, have been developed. Synergistic effects between their components provide these materials with exciting properties for light harvesting and charge separation, fundamental issues in artificial photosynthesis. Therefore, the development of new hybrid multifunctional photocatalysts using sunlight to produce fuels and chemicals is considered as a cornerstone for CO_2 valorisation technologies.

In this work we report different strategies and modifications photocatalysts to increase process performance. The modification of optoelectronic properties of through the use of band gap engineering strategies, allow controlling the absorption of incident photons, redox capabilities and subsequently the photocatalytic performance. In addition, metal nanoparticles act as electron scavenger and as co-catalyst [2-3].

On the other hand, the use of novel hole transport materials maximize the light harvest and charge separation. On the other hand, efforts are devoted to shed light on mechanistic aspects of the reaction. In order to clarify the effect of different parallel and competitive reactions in the activity and products distribution, a series of photocatalytic experiments in combination with operando characterization using synchrotron radiation and laboratory techniques and theoretical calculations were performed.

These studies show that introduction of SPR NPs as co-catalyst or conductive polymers as hole transports leads to changes in the conversion and enhanced selectivity to higher demand electron products, such as CH_4 , while the CO and H_2 concentrations decrease.

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Keywords: Solar Fuels, Photocatalysis, Reaction Mechanism

MS19-P10

X Ray study of GZO thin films

Beatrice Gabriela Sbarcea¹, Petronela Prepelita², Lucia Nicoleta Leonat³

- Advanced Materials Department National Institute for R & D in Electrical Engineering ICPE-CA, Splaiul Unirii Street, Nr. 313, District 3, 030138, Bucharest, Romania
- Laser Department National Institute for Laser, Plasma and Radiation Physics, 409 Atomistilor Street, PO Box MG-36, 077125, Magurele, Romania
- Department: Laboratory of Multifunctional Materials and Structures - National Institute of Materials Physics, Atomistilor Str., No. 405A PO Box MG 7, 077125, Magurele, Romania

email: gabi_bea@yahoo.com

Ga:ZnO thin films (GZO) are studied in order to achieve good characteristics for optoelectronic devices. The purpose of this paper is to study the thin films proprieties grown by Pulsed Laser Deposition. Doped ZnO thin films were characterized structural and optical. X-ray diffraction measurements reveal a polycrystalline structure of films and doped ZnO films exhibit hexagonal wurtzite crystal structure. Thin films thicknesses are around 160 nm - 680 nm. The optical transmittance of GZO thin films is over 70%, which indicates possible applications for optoelectronic devices. Pulsed laser deposited for n-type transparent ZnO can be applied to optoelectronic devices in order to replace the conventional ITO and AZO films.

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Keywords: GZO, optoelectronic devices, thin films

$Ce_{0.8}Gd_{0.2}O_{2\cdot\delta}$ / $La_{0.6}Sr_{0.4}CoO_3$ heterostructures prepared by pulsed laser deposition

Lucía dos Santos Gómez¹, José Manuel Porras Vázquez¹, Enrique Ramírez Losilla¹, David Marrero López²

- Departamento de Química Inorgánica, Cristalografía y Mineralogía. Universidad de Málaga., Málaga, Spain
- Departamento de Física Aplicada I. Universidad de Málaga., Málaga, Spain

email: lucia 2 santos@hotmail.com

Oxide interfaces have received greater attention due to the possibility to obtain properties that are very different from bulk materials. Due to the wide variety of electronic and ionic phenomena than can be detected at the interfaces, such materials have many technological applications [1]. Attention is being drawn to oxide heterostructures, a new family of artificial materials where electronic and ionic properties can be modulated at the interfaces by varying the characteristics of the layers [2, 3]. Slight variations in the near anionic-cationic order might take place if there exists strained interfaces. The interest in multilayared heterostructures derives from the mobility deffects and the space-chargezone effects at the interfaces. In addition, a new degree of freedom related to the capacitive and resistive contributions is provided as a consequence of the size effects of these artificial structures.

In the present work, for the first time, we investigate the structure, microstructure and electrical properties of a new family of heterostructured materials with alternated thin layers of La_{0.6}Sr_{0.4}CoO₃ (LSC) and Ce_{0.8}Gd_{0.2}O_{2.6} (CGO) deposited by pulsed laser deposition on (110) NdGaO₃ (NGO) single crystal substrates. In order to evaluate the interfacial contribution to ionic-electronic conductivity and know what is actually happens at the interface of MIECs, different heterostructures were prepared by varying both the number of bilayers (N) and the total thickness of the samples (N = 2 and 5; and the thickness were 50, 100 and 300 nm).

The quality of the samples was examined by HR-TEM and all of them presented well defined interfaces. The rocking curve and HR-TEM images indicate that the CGO cells are rotated 45° with respect to NGO and LSC ones as can be observed in the figure. In addition, due to the great lattice mismatch between NGO, CGO and LSC, the asymmetric reflections of (113) plane can be distinguished in the reciprocal space mapping and the analysis of these results indicates that the interfaces generate a compressive strain in CGO layers and, consequently, tensile strain in the LSC ones. Conductivity of CGO/LSC heterostructures is affected by the thickness and the number of interfaces in the heterostructure, and the thickness is the dominant factor in the conductivity variation.



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Keywords: Heterosturctures, Ce_{0.8}Gd_{0.2}O₂₋₈, La_{0.6}Sr_{0.4}CoO₃₋₈

MS20- Rating and improving data quality: instrumentation, analysis and postprocessing

Chairs: Dr. Karine Röwer, Dr. Loes Kroon-Batenburg

MS20-P01

Structurefinder

Daniel Kratzert

1. Albert-Ludwigs-Universität Freiburg, Inorganic Chemistry, Freiburg im Breisgau, Germany

email: daniel.kratzert@ac.uni-freiburg.de

Databases like the Cambridge Structural Database or the Crystallographic Open Database are good at collecting information from crystallographic experiments and making it searchable. But to my knowledge, there is no easy-to-use software to find and present the results of crystallographic experiments for a single workgroup.

Presented is a new computer program called StructureFinder. It creates a database of crystallographic structures on a computer and makes them searchable. The program can search for various properties: Unit cell, free text, creation date, included atom types and space group. To build the database, StructureFinder collects all computer information files (cif file format) below certain directorys on a hard disk. The containing information is stored into a SQLite database. The database can be accessed by two different interfaces. A stand-alone Qt program (figure 1) to install on a single computer or a web interface (figure 2) to be accesses by a whole work group.

StructureFinder greatly enhances the ability to find old structures in huge collections of crystallographic datasets. The program can easily handle more than 10.000 structures. It can be downloaded at <u>https://www.xs3.uni-freiburg.de/</u>research/structurefinder.

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Keywords: structure search, unit cell, cif files

MS20-P02

Low-cost portable devices for inert lowtemperature sample manipulation

Nils Trapp¹, Michael Solar¹, Michael Wörle¹

1. Small Molecule Crystallography Center, ETH Zürich, Zürich, Switzerland

email: nils.trapp@org.chem.ethz.ch

Sample cooling has become widely implemented in crystal structure determination, due to the broad array of advantages it offers (Goeta & Howard, 2004). In particular, measurement at reduced temperatures can severely improve data accuracy and resolution for small molecule crystals, due to reduced and more isotropic atomic vibration (Brock & Dunitz, 1990). In addition, it can reduce radiation damage in protein crystals, enable variable temperature or phase transition studies and allow measurements of samples that are not stable or solid under ambient conditions. Low temperature can also prevent crystal damage due to the escape of co-crystallized solvent, which often retains a relatively high vapor pressure. Because the cooling medium used in open-flow sample cryostats is either nitrogen or helium gas, air-sensitive and even pyrophoric crystals can be measured using standard equipment. However, transferring sensitive samples from storage vessel to diffractometer, without compromising crystal and data quality, remains a challenge in many cases.

A straightforward procedure for preparing and mounting crystals under inert conditions is demonstrated, using a specialized apparatus (μ CHILL). The technique is extremely flexible, requiring only a single operator, little practice and almost no preparation time. The device enables a wide temperature range (at least -60 °C to room temperature), providing temperature control and very stable conditions with no ice formation over extended time periods. The flexible, modular and low-cost design is based on 3D printed parts and readily available standard components, potentially making the device available to a wide range of users and applications not limited to single crystal studies.

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Keywords: crystal mounting, instrumentation, cryocrystallography

Scope and limitations on refinement strategy. service crystallographer's publishing woes

Arkady Ellern1

 Chemistry Department. Iowa State University, Ames, Iowa, United States of America

email: ellern@iastate.edu

Small molecule X-Ray structure determination can be considered as a three step process where each step is dependent the previous one.

Data collection. All special techniques (unstable samples, low temperature, high pressure experiments etc.) were well established many years ago. The revolution in computing during the last two decades speed up this step significantly as modern diffractometers with power radiation sources can collect full-sphere data with high redundancy in a few hours. As a result this step nowadays is absolutely routine in all specialized facilities.

Structure Solution/Refinement. "Black-box", like Bruker EXPRESSO, obtains good results for simple samples by users without sufficient background in symmetry, crystallography, diffraction, refinement and even chemistry. However, in real life the majority of structures must be resolved unambiguously only by experienced professionals to consider the best route and final point of analysis, which is not always obvious and beyond a reasonable doubts.

As an example, giant spherical keplerate cluster structures like $\{Mo_{72}V_{30}\}$ require a lot of restrains to model the disorder during the refinement to hold outer and inner ligands at reasonable positions and with acceptable temperature factors. The concomitant difficulties are: the split positions for metal core, the huge voids filled with diffused water solvent, uncertainties in the valence state of metals and occupancy of counter-ions. Where is the limit of data "massaging" and "fixing" on the way of supporting our model of choice? Where should we stop?

Majority of customers use X-Ray structure determination for the qualitative and quantitative analysis which means they are fully satisfied with the connectivity table to assure the synthetic path and the proof of obtaining the target substance. How far should we go with such structures? The refinement for the simple metallo-organic complex can illustrate how stepwise split of disordered benzene solvent position influence the geometrical and thermal parameters of the main cluster.

Publication. Can we trust old X-ray structural results even though they can hardly pass the new strict requirements for publication? How many different expert opinions can we have on one simple structure like $[Cr_3(C_3H_5O_{2,0}O(H_2O)_3]$ $NO_3 \times 0.5H_2O$ and what is wrong with publishing questionable (or even unintentionally wrong) results? Should we still describe the structure in a paper if we must supply CIF with all intensity/refinement data? Why one might still consider service crystallographer as a valuable co-author of publication? Let us try to get a consensus on those and some other questions

Keywords: refinement, publication, checkcif

MS20-P04

Shine bright like a diamond: microfocus X-ray sealed tube sources with diamond hybrid anode technology

Juergen Graf¹, Tobias Stuerzer², Holger Ott², Paul Radcliffe¹, Carsten Michaelsen¹

1. Incoatec GmbH, Geesthacht, Germany)

2. Bruker AXS GmbH, Karlsruhe, Germany

email: graf@incoatec.de

Diamond exhibits several unique properties, such as high thermal conductivity, low thermal expansion, extreme hardness, chemical inertness and a fairly high transmission coefficient for X-ray radiation. The thermal conductivity of diamond is about 5 times higher than that of copper and the highest known conductivity of all bulk materials [1]. Therefore, diamond, being a non-toxic material, is increasingly replacing traditional materials for the thermal management in challenging applications where a high local heat load needs to be dissipated, such as in heat sinks for high-power microelectronic devices.

The high transmission coefficient, even at low X-ray energies, fosters the use of diamond in X-ray components such as carrier membranes in X-ray lithography or X-ray windows. In X-ray sources, diamond can be used as a transparent heat sink directly coupled to the anode material. This improves the heat dissipation considerably and allows for an increase in tube brilliance by applying a higher power load on the anode.

The IuS DIAMOND is a new type of microfocus sealed tubes using a unique anode technology, the diamond hybrid anode. It takes advantage of the exceptional high thermal conductivity of diamond by using a bulk industrial diamond as a heat sink, which is coated with a thin layer of the target material, such as Cu. Mo or Ag. The diamond heat sink makes the heat dissipation in a diamond hybrid anode more efficient. Consequently, the IµS DIAMOND can accept a higher power density in the focal spot on the anode without damaging the surface of the target layer. The balanced heat management in the source assures that the intensity loss over time is only a few percent over 10,000 h of full power operation, which is significantly lower than the intensity degradation observed for microfocus rotating anodes [2,3]. Therefore, the intensity of the IµS DIAMOND is about 20% higher than the average intensity output of a modern microfocus rotating anode.

The I μ S DIAMOND establishes a new class of X-ray sources, combining an intensity output that exceeds the average intensity of a microfocus rotating anode with all the comfort and lifetime of a standard microfocus sealed tube with a bulk anode. In this presentation, we will be discussing the main features of the I μ S DIAMOND and presenting selected results to demonstrate the impact of this new class of microfocus sealed tube X-ray sources on the data quality for applications, such as protein and small molecule crystallography.

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Keywords: X-ray Source, Diamond, Instrument Development

MS20-P05

Integrated crystallographic services at EMBL-Hamburg

Saravanan Panneerselvam¹, Gleb Bourenkov¹, Guillaume Pompidor¹, Isabel Bento¹, Johanna Hakanpää¹, David Von Stetten¹, Maria Garcia Alai¹, Thomas R. Schneider¹

1. EMBL-Hamburg, Hamburg, Germany

email: saravanan.panneerselvam@embl-hamburg.de

EMBL Hamburg is operating three beamlines (P12 for small-angle X-ray scattering 'SAXS', P13 and P14 for macromolecular crystallography 'MX') on the PETRA III storage ring at DESY (Hamburg, Germany). The beamlines are embedded in the Integrated Facility for Structural Biology which - in addition to the X-ray experiments on the beamlines - offers facilities and services for sample preparation and characterization and for data analysis.

By using the highly brilliant X-ray beam produced by PE-TRA III, beamlines P13 and P14 enable X-ray diffraction experiments on the most challenging crystals:

- small (< 100 μm^3) crystals can be exploited using micro-focused X-ray beams and serial crystallography strategies
- optimum data can be extracted from large crystals with a highly parallel large beam.
- phasing is facilitated by a high photon flux at low X-ray energies
- diffraction from large unit cells (> 1000 Å) can be resolved
- data from fragile crystals can be collected *in situ* in CrystalDirect[™] plates
- For pump-probe experiments, a dedicated endstation is under construction on P14.

For less challenging cases, a highly automated and integrated environment is in place for high-throughput data collection.

The Sample Preparation and Characterization facility (SPC) provides an entry point for protein samples which still need to be tested and prepared for use in SAXS and/or MX. A suite of biophysical protocols is available to evaluate the suitability of user-supplied samples; preparative techniques can then be applied to optimize samples for crystallization. For crystallization, high-end equipment is in place that can be accessed remotely via the web-based CRIMS system. A CrystalDirect system has been installed for automated crystal harvesting and a dedicated derivative lab is available for users for derivatization experiments.

Various modes of access are available (For details, please visit: www.embl-hamburg.de):

- · competitive: P13 / 14
- collaborative: P13 / P14
- · EU-supported (iNext): P13 / P14 / SPC
- fee for service (academic / industrial): P13 / P14 / SPC

We will describe the user-accessible facilities, examples of projects 'from protein to structure', experimental highlights, and the available access modes.

Keywords: beam lines,micro crystallography, integrated facility

Misplaced hydrogen atoms and undetected disorder in imidazoles and pyrazoles

Carl Schwalbe¹, Peter Wood², Andrew Maloney², Suzanna Ward²

- School of Life & Health Sciences, Aston University, Birmingham, United Kingdom
- 2. Cambridge Crystallographic Data Centre, Cambridge, United Kingdom

email: carlschwalbe@hotmail.com

Imidazole (Im) and pyrazole (Pyzl) rings occur in drugs such as cimetidine and celecoxib. The Im ring of histidine is important in biological systems since it often participates in proton relays. The NH group of one neutral Im or Pyzl ring frequently hydrogen bonds to N of an adjacent ring; the similarity of electron density between NH...:N and N:... HN muddles the assignment of protonation sites. Geometrical criteria can be more reliable.

Malinska et al. [1] developed criteria for the protonation state of histidine. Differences in bond length between C-NH and C=N, along with differences in bond angle between C-NH-C and C=N-C were most significant. A precise neutron diffraction study at 103 K of Im [2] gave 1.347, 1.322 Å and 107.1, 105.1°. A search of the 2018 version of the CSD for non-fused neutral Im rings in organic structures with R <= 10% and no recognized disorder yielded 547 hits with 478 unique refcodes. The mean difference DISDIF between C-NH and C=N bond distances was 0.024(12) Å; between C-NH-C and C=N-C angles (ANGDIF), 2.3(8)°. In 5 structures both differences are < -0.01 Å and $< -0.8^{\circ}$, implying that the H atom has been misplaced. Alterations are suggested. For a sizeable number of structures both differences have small absolute values, suggesting previously undetected NH/N disorder.

A similar search for Pyzl structures yielded 723 hits, 635 unique. Pyzl itself with Z' = 2 is not a totally reliable guide to geometry: a comprehensive variable-temperature study [3] showed small amounts of charge transfer from one ring to another and NH/N disorder. Their structure determination at 100 K gave, for the independent molecules, C-NH and C=N distances of 1.338, 1.334 and 1.347, 1.330 Å, C-NH-N and C=N-NH angles of 112.2, 104.2 and 112.2, 104.5°. Notwithstanding the closeness of bond distances, the differences in bond angles are unmistakeable. Nine structures have DISDIF < -0.01 Å and ANGDIF < -3.3°, implying that the wrong N atom has been protonated; 5 are corroborated by CheckCIF Alerts for clashes. Most symmetrically substituted Pyzl structures have 50:50 NH/N disorder, and the prevalence of smaller ANGDIF values suggests widespread partial disorder.



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Keywords: imidazole, pyrazole, hydrogen positions

The benefits of K_B radiation

Michael Bodensteiner1, Tobias Mayr2

- 1, X-ray Crystallography, Faculty of Chemistry and Pharmacy, University of Regensburg, Regensburg, Germany
- Faculty of Chemistry and Pharmacy, University of Regensburg, Regensburg, Germany

email: michael.bodensteiner@ur.de

K₈ is much weaker in intensity than K_a and therefore practically not used for single crystal diffraction experiments. Most X-ray labs are equipped with Mo-K, and Cu-K, sources, but in some cases an intermediate wavelength would be desirable. Such a compromise can be provided by Cu-K_B radiation ($\lambda = 1.39$ Å). Compared to Cu-K_a ($\lambda = 1.54$ Å) the amount of available data is increased by more than 35 per cent and the absorption significantly lowered. This can also be achieved with Mo-K_a ($\lambda = 0.71$ Å), but the quantum efficiency of the diffraction is much higher for Cu-K_B. Another general advantage of K_B radiation compared to K_a is the absence of α_1/α_2 splitting at higher diffraction angles. This leads to a relative improvement of the $I/\sigma(I)$ at higher resolution. Our investigations have shown that in many cases almost identical or even better quality structures could be obtained by using the Cu-K_β wavelength compared to either Mo-K_n or Cu-K_n. We even encountered some structures that could only be refined properly when Cu-K 8 data was applied.[1]

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Keywords: K-beta radiation, wavelength, data quality

MS20-P08

EuPRAXIA – a compact, cost-efficient XFEL source

Maria Weikum1, Paul Andreas Walker1, Ralph Assmann1

1. Accelerator R&D, Deutsches Elektronensynchrotron (DESY), Hamburg, Germany

email: maria.weikum@desy.de

(on behalf of the EuPRAXIA collaboration)

One of the main limitations for crystallographic studies – whether it be in structural biology, chemical analysis or material science – is the availability of suitable diagnostic instruments which are to-date typically found in the form of large accelerator-based facilities, such as Free-Electron Lasers (FELs), synchrotron storage rings or accelerator-based neutron sources.

With the Horizon 2020 project EuPRAXIA ("European Plasma Research Accelerator with eXcellence In Applications") we want to present a possible approach towards solving this research bottleneck through the use of novel compact accelerator technology. Currently in its conceptual design phase, the future EuPRAXIA facility will centre around a multi-gigaelectronvolt plasma-based electron accelerator delivering industrial-grade beam quality. Radiation sources will be available in the form of a Free-Electron Laser in the single nanometre to sub-nanometre wavelength range as well as more compact radiation generation schemes tunable in the UV to gamma-ray regime. Compact positron and neutron sources are foreseen as possible additional features. Thanks to the utilized plasma accelerator technology, the generated beams will be intrinsically ultrashort - on the order of single to tens of femtoseconds in duration - as well as small in transverse size - down to single micrometres. This makes them highly suitable as probe beams for various applications, including time-resolved studies and pumpprobe experiments.

One of the main aspects that will set EuPRAXIA apart from conventional instruments of the same class is a considerable reduction in size and cost due to its smaller design. It will thus not only provide a novel analytical instrument, but will also present, beyond that, a first European prototype facility paving the way towards future cost-effective, compact light and particle sources.

Keywords: X-ray source; particle beam source; compact XFEL

Results and experience using recycled beam at the CXI instrument of LCLS

Mark Hunter¹

1. LCLS at SLAC National Accelerator Laboratory, Menlo Park, United States of America

email: mhunter2@slac.stanford.edu

Beam time at X-ray Free Electron Lasers (FELs), such as the Linac Coherent Light Source (LCLS), is currently oversubscribed several fold. At LCLS, multiplexing has been used to increase access by using a monochromator to extract a 0.5 or 1 eV slice of the pink beam bandwidth (~50 eV) and deliver it to a different experiment; this setup is commonly used for multiplexing of the monochromatized beam at X-ray Pump Probe (XPP) and Coherent X-ray Imaging (CXI) instruments. However, many experiments at CXI utilize a small fraction (< 50%) of the incident beam due to a combination of small scattering cross sections and < 50 µm path lengths. Therefore a new chamber and re-focusing optics were designed to make use of the transmitted beam from a primary experiment at CXI. The Serial Sample Chamber (SSC) was commissioned in July of 2016 and started parasitic operations immediately, contributing to single-wavelength anomalous difference (SAD) protein crystallography experiments conducted the same month. Since its successful commissioning, in-house experiments and user experiments have been conducted in SSC, expanding the amount of available beam time to the community. Starting in 2017, SSC became the dedicated place for the Protein Crystallography Screening (PCS) program at LCLS. Results from using SSC for experiments and the quality of the recycled beam will be discussed including discussions of the challenges facing the parasitic experimental setup. The serial data collection setup will soon be implemented at European XFEL at the SPB/SFX instruments.

Keywords: Crystallography, X-ray FEL

MS20-P10

Interaction of non-ideal, multicomponent solid solutions with water: a simple algorithm to estimate final equilibrium states

Rosa María Rodríguez Galán¹, Manuel Prieto¹

1. Department of Geology. University of Oviedo, Oviedo, Spain

email: rosa@geol.uniovi.es

Interaction of minerals with water frequently yields dissolution-coprecipitation processes in which foreign ions incorporate into the solid structure substituting for the major ion. By this way, coprecipitation often controls the transport and fate of harmful ions in the environment and can be exploited for environmental remediation.

Geochemical modeling and experimental studies of these aqueous - solid solution (AQ~SS) processes are typically performed using pure minerals. However, the host minerals could be binary solid solutions and the study of their interaction with a third dissolved ion would require considering ternary solid solutions (TSS). The first step in modeling coprecipitation processes is providing the equilibrium state to which a specific AQ-SS system will tend to react. However, computer codes like PHREEQC does not deal with non-ideal ternary or higher order solid solutions and GEM-Selektor [Wagner et al., 2012; Kulik et al., 2013] is the only modeling code that allows calculating equilibrium in AQ-SS systems that involve non-ideal multicomponent solid solutions. We have implemented a simple algorithm (AQ-TSS) to work in a PHREEQC context via the BASIC interpreter tool of this modeling code. AQ-TSS estimate equilibrium in AQ-SS systems involving non-ideal ternary solid solutions (regular, subregular, or any-type). The (Pb,Sr,Ba)SO4 solid solution is used as example system. The three binary joints are considered separately. Non-regular solid solutions are treated by combining a set of regular models defined for specific ranges of composition and neglecting ternary interactions, which represent a minor contribution when two of the three components occur in minor amounts. Such a scenario is realistic for ambient temperature processes in which the host solid solutions exhibit wide miscibility gaps and the dissolved metal occurs in trace or minor amounts. The algorithm has been tested by comparing the results obtained by AQ-TSS with those obtained using PHREEQC with the same binary non-ideal solid solutions and by reproducing some calculations performed by Vinograd et al. (2013) using GEMS (Kulik et al., 2013). The results obtained by AQ-TSS and PHREEQC are virtually equal. The results obtained using GEMS are of the same order of magnitude, the difference (~5%) being reasonable given the different basis involved in both algorithms.

The extension to non-ideal solids solutions of higher order is feasible, but the formulations become bulkier with each added component. The lack of rigorous experimental data involving aqueous-ternary solid solution systems is a major obstacle and a challenge for future research.

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Keywords: Solid Solution. Coprecipitation. Computer modelling

MS20-P11

The HyPix-6000HE detector – no photon left behind

Fraser White¹, Dyanne Cruickshank¹, Alex Stanley¹, Damian Kucharczyk², Mathias Meyer²

1. Rigaku Oxford Diffraction, Chalgrove, United Kingdom 2. Rigaku Oxford Diffraction, Wroclaw, Poland

email: fraser.white@rigaku.com

Collecting datasets which are high quality yet efficient for a wide range of sample types and crystal quality is a key requirement of many diffractometer users around the world. Access to equipment which meets this requirement can enable high throughput, provide better data quality or open up new areas of research. One component of such a high throughput diffractometer is the detector. Here we will explore the use of a hybrid photon counting detector to enhance data collection capabilities of modern diffractometers.

Hybrid Photon Counting (HPC) detectors have established themselves as the detector of choice for synchrotrons and where the highest quality of data is a requirement due to their direct detection of X-rays, zero readout noise and high speed. The HyPix-6000HE detector is a HPC detector designed and produced by Rigaku. HPCs are scintillator-free by design, which allows for true digital photon counting. This means that X-ray photons are counted as soon as they arrive at the detector with no approximation of counts from integrated charge and no conversion of X-ray photons to light photons with the requisite addition of noise. Additional features such as energy discrimination, a zero dead time mode and 100 Hz frame rates are also enabled by the technology present in the HyPix-6000HE detector.

A photon-counting, large-area detector – PHOTON III

Michael Mrosek¹, Martin Adam¹, Bruce Becker², Roger Durst¹, Joerg Kaercher²

Bruker AXS GmbH, Karlsruhe, Germany
 Bruker AXS Inc., Madison, United States of America

email: michael.mrosek@bruker.com

The appearance of significantly stronger third generation synchrotron sources at large scale facilities and microfocus technology using in-house sources has led to the replacement of imaging plates by CCD, CMOS and HPAD detectors. Current state-of-the-art HPAD detectors, such the PHOTON II, deliver impressive results and have allowed the collection of the first in-house GPCR structure only a few months ago.

Modern synchrotron beamlines show a preference for largest possible detectors, which provide a number of advantages:

- Increased sample-detector distance results in reduced background X-ray scattering with improved signalto-noise measured from weakly diffracting samples
- More reflections are collected per frame, reducing the radiation dose and overall measurement time
- Efficient collection of complete data at high resolution
- Better signal separation from reflections of very long unit cell axes

The Detective Collection Efficiency (DCE) is an established measure to describe the productivity of an X-ray detector[1]:with Ω being related to the active area size, DQE to the sensitivity of the detector and t_{read} to the read out dead time unit. The new PHOTON III is a detector for structural biology, which improves the DCE from two ends:

- The detector has a large active area of 280 cm², resulting in a DCE two-times greater than the PHOTON II
- The detector is operated in a newly developed photon counting mode.

The PHOTON III offers large active-area detectors to the home laboratory at affordable costs. Like all our CPAD detectors the PHOTON III has zero read out time, does not suffer from charge charging effects and satisfies the Shannon-Nyquist theorem. Even better, this goes along with a remarkable improvement in background suppression using the newly developed photon counting mode.

Apart from a discussion of technical details the presentation will focus on first data sets collected with the new detector.

$$DCE = \frac{\Omega}{4\pi} DQE \left(1 + \frac{t_{read}}{t_{frame}}\right)^{-1}$$

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MS20-P13

Highest Data Quality with Latest In-House Sources and Detector Technology

Holger Ott¹, Tobias Stuerzer¹, Michael Mrosek¹, Michael Ruf², Bruce C. Noll², Matthew Benning², Martin Adam¹, Juergen Graf³

- 1. Bruker AXS GmbH, Karlsruhe, Germany
- 2. Bruker AXS Inc., Madison, United States of America
- 3. INCOATEC GmbH, Geesthacht, Germany

email: holger.ott@bruker.com

Modern chemical and biological crystallography continuously pushes the limits to ever smaller samples with typically weaker diffraction properties. Here we will present a number of structures obtained from extremely challenging samples. Experimental data collected on an in-house system illustrate the strength of two new components which tremendously improve the performance of laboratory instrumentation: the new ImS DIAMOND source and the new PHOTON III X-ray detector.

The air-cooled ImS DIAMOND microfocus sealed tube source uses a unique diamond hybrid anode technology to produce intensities similar to modern microfocus rotating anodes. The anode consists of a diamond substrate coated with copper. The high thermal conductivity, low thermal expansion and extreme hardness of diamond make it an ideal substrate, which allow for higher power loading and greater long-term stability of the source, delivering the brightest micro-focus sealed tube ever.

As of today another problem associated with high-end X-ray sources is gone: high maintenance costs. The ImS DI-AMOND does not require any routine maintenance and has the same legendary life time which makes the ImS system the most popular microfocus X-ray source for more than a decade.

The PHOTON III is a new CPAD (charge-integrating pixel array detector), which utilizes a mixed-mode approach for data collection. The weak reflections are measured in photon-counting mode and the strong reflections are measured in integrating mode. Consequently, the ultra-sensitive PHO-TON III detector can collect very weak reflections without suffering from charge-sharing or non-linearity effects common to other photon-counting detectors.

Bruker's D8 QUEST and D8 VENTURE both take advantage of these improvements in source and detector technology, leading to a previously unknown level of performance without increasing operational costs.



MS21- Intermolecular interactions from structural, energetic and charge density perspective(s)

Chairs: Prof. Enrique Espinosa, Prof. Ulli Englert

MS21-P01

Crystal structure and reconstruction of charge density of 9-aminoacridine hemihydrate

Sylwia Pawlędzio¹, Anna Makal¹, Damian Trzybiński¹, Krzysztof Woźniak¹

1. University of Warsaw, Department of Chemistry, Biological and Chemical Research Centre, Warsaw, Poland

email: spawledzio@chem.uw.edu.pl

Nowadays, the most routine X-ray structure determination in crystallography is based on so-called Independent Atom Model (IAM) of electron density, which assumes both sphericity and neutrality of the atoms. Unfortunately, the quantitative topological analysis of an electron density based on IAM is inaccessible (Dittrich et al., 2009). The multipolar approach, as proposed by Hansen and Coppens, (Coppens, 1997), is the method of choice in modelling of the experimental electron density distribution. High-resolution diffraction data of outstanding quality are mandatory in order to perform full structure refinement with multipolar model - a condition impossible to meet for very small crystals or macromolecules. However, the theoretical databanks of aspherical scattering factors developed in recent years, for example, UBDB databank (Jarzembska & Dominiak, 2012) based on experimental geometries, can be used in order to reconstruct the charge density with the Transferable Aspherical Atom Model (TAAM) approach.

Acridines belong to the polycyclic heteroaromatic chemical compounds and their derivatives have found a wide range of applications in clinical area as an antimicrobial, antiviral or antitumor agents as well as in chemical analysis, for example as a matrix for matrix-assisted laser desorption/ ionization (MALDI). The 9-aminoacridine can be considered as a model compound from this family of chemicals. In its neutral form it crystallizes as a hemihydrate the $I 4_1/a$ 2/c 2/d space group with several atoms in special positions. The very interesting crystal structure of title compound was described in the 1983 year by Chaudhuri and until now has not been more thoroughly investigated. Here, the reconstruction of charge density distribution with the UBDB data bank and TAAM refinement will be performed in order to obtain more accurate geometry of the compound, the quantitative topological analysis of an electron density as well as the basis for the energetic calculation (crystal lattice and dimer energies) by using Crystal, CrystalExplorer or Pixel approaches. This research is the part of the wider project carried out in cooperation with dr Mihails Arhangelskis.

Acknowledgments:

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Keywords: 9-aminoacridine hemihydrate, charge density, TAAM refinement

MS21-P02

Preparation of non-covalent organic frameworks using dodecasubstituted porphyrins

Keith Flanagan1, Mathias O. Senge1

 School of Chemistry, Trinity College Dublin the University of Dublin, Dublin, Ireland

email: kflanaga@tcd.ie

Nowadays the use of porphyrins to create highly porous, sponge-like frameworks is a well-studied field, established by the seminal work of Byrn et al. coining the phrase "porphyrin sponge" in 1991.[1] This initial study used a porphyrin host, trapping a variety of guests within the crystal lattice. Since then, many contributions have focused on the manipulation of planar porphyrins containing a variety of functional groups (namely carboxylic acids or halogens) to obtain directly linked porphyrin frameworks.^[2] However, as of yet, there are no specific examples of the use of highly distorted porphyrins [3] being used to obtain such highly porous materials. In this work, we have synthesized a series of 5,10,15,20-tetraaryl-2,3,7,8,12,13,17,18-octaethylporphyrins with alternating halogen, alkyl, and aryl substitution patterns to probe the effects of non-planarity on the formation of non-covalent organic frameworks.

The target porphyrins were synthesized according to a modified Lindsey condensation reaction followed by metal(II) insertion. To investigate substituent interactions, modified aldehydes were used. For halogen effects, a family of derivatives with F, Cl, Br or I in either the ortho- or para-position of the meso-aryl residues were selected. Hydrogen bonding interactions were examined by incorporating a nitrile group. Steric effects were examined through the incorporation of a benzyloxy group at either the meta- or para-positions. Finally, investigations were conducted into the use of arm-extended porphyrins using a triazole linker group to further extend their functionality. Solid-state structures were determined via small molecule X-ray crystallography to elucidate the major distortion modes and to characterize any non-covalent interactions. These were then compared to their planar derivatives to determine effects the substitution patterns may have on the formation of non-covalent organic frameworks.



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Keywords: Porphyrin, Halogens, Macrocycles

MS21-P03

Intermolecular interactions in the cyanuric acid dihydrate on the basis of experimental charge density

Barbara Gruza1, Paulina Dominiak1, Damian Trzybińsk1

1. Biological and Chemical Research Centre, Department of Chemistry, University of Warsaw, Warsaw, Poland

email: barbara.gruza@student.uw.edu.pl

The structure of anhydrous cyanuric acid, its intermolecular interactions and thermal parameters have been described in 1971 by G.C. Verschoor [1]. In the following years, i.a., strong donor-acceptor interactions connected with occurrence of N–H and C=O functional groups were investigated by T.C. Lewis [2] for the anhydrous form as well for readily formed solvates and co-crystals. Possibility of satisfying all the hydrogen bonding functionalities and it's influence on the crystal structure were verified.

I am presenting experimental charge density analysis for the cyanuric acid dihydrate. Electron density distribution was described with Hansen and Coppens pseudoatom model. Crystal structure, occurring interactions and vibrational parameters were compared with periodic theoretical calculations both for dihydrate and anhydrous form. Molecular interactions with water molecules were also justified basing on the TGA/DSC measurements.

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Keywords: cyanuric acid dihydrate, intermolecular interactions, charge density

MS21-P04

Hierarchy and the nature of intermolecular interactions in systems containing aromatic N-heterocyclic rings

Tomasz Sierański1

1. Lodz University of Technology, Institute of General and Ecological Chemistry, Łódź, Poland

email: tomasz.sieranski@p.lodz.pl

Non-covalent interactions involving N-heterocyclic aromatic rings have recently received greater attention. They play an important role in many chemistry-related fields such as structures of biomolecules, the reactivity of molecules, crystal engineering, molecular recognition, and nanoengineering. Such rings, because of their distinctive electronic properties, are involved in different interaction patterns including π -stacking and hydrogen bonds. Hence, they are considered as useful recognition elements in many biological systems and became key components in most known drug molecules [1, 2].

Though some significant progress has been definitely made in the study of interactions involving N-heterocycles, most studies only focus on analyzing of stationary geometries and say nothing of a whole range of many other configurations. Accurate potential energy surfaces (PES) of such systems are not available and it is impossible to see how the stability of a particular system changes along with various geometrical parameters. Such maps, if they were present, would literally give a new way to look into the interactions patterns that may be formed.

For this reason, the extremely extensive analysis of potential energy surfaces of model N-heterocyclic dimers has been performed. The interaction energies of hundreds of thousands of dimers have been calculated. As the studied N-heterocycles the following ones have been selected: pyrrole, purine, pyridine, imidazole, pyrazole, 1,2,3-triazole, and 1,2,4-triazole. Since the interaction energies of a large number of systems were to be calculated, all the calculations have been carried out using a dispersion-corrected density functional. Other calculations, such as natural bond orbital and energy decomposition, have also been applied. The obtained results were then related to the statistical analysis made on the data gathered from Cambridge Structural Database [3].

The appliance of multidimensional analysis provides much deeper insight into the "landscape" of the interaction energies of the particular systems and enables one to see "a bigger picture" of what really occurs. The performed study, involving the combination of many different methods, has revealed the complexity of the formed intermolecular interactions. Apart from providing a "literal new look" into the present interaction patterns, another picture has emerged. Intermolecular interactions, especially stacking, present in the studied N-heterocycles, are seen" as a combination of many different sources of the interaction energy. The presented results may be a key importance in a prediction of crystal structures and may find a use in modeling of a crystal possessing desired properties.

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Keywords: intermolecular interactions, density-functional theory, cambridge structural database

MS21-P05

Understanding disorder in a Z'=4 structure with computationally cheap tools

Christophe Vande Velde¹, Wim Van Beek², Kourosch Abbaspour Tehrani²

- 1. University of Antwerp, Faculty of Applied Engineering, Advanced Reactor Technology, Antwerpen, Belgium
- 2. University of Antwerp, Department of Chemistry, Orsy, Antwerpen, Belgium

email: christophe.vandevelde@uantwerpen.be

As computationally cheap tools have recently become available to better understand crystal packing, we have applied the CE-B3LYP method as implemented in Crystal Explorer 17 [1] to an interesting structure with Z'=4, and whole molecule disorder in each of the four molecules in the asymmetric unit.

The structure itself contains many subtle features which are interesting to discuss all by themselves, but we are interested to see whether the energy calculations will aid in providing a reasonable explanation why the structure crystallizes as it does.

The average nature of the coordinates obtained from the crystallographic experiment will obviously be the largest challenge, as it conflicts with the basic premise of a calculation that does not optimize the atomic coordinates before calculating energies.



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Keywords: whole molecule disorder, crystal explorer, high Z'

MS21-P06

New models of electron density for electrostatic interaction energy estimation

Slawomir Bojarowski¹, Paulina M. Dominiak¹, Prashant Kumar¹, Claudia M. Wandtke², Birger Dittrich³

- 1. University of Warsaw, Faculty of Chemistry, Warsaw, Poland
- 2. Institut fur Anorganische Chemie Georg-August-Universitat, Goetingen, Germany
- 3. Anorganische Chemie und Strukturchemie, Heinrich-Heine Universitat, Dusseldorf, Germany

email: sbojarowski@chem.uw.edu.pl

The accurate estimation of electrostatic interaction energies in a reasonable time is a still challenging task. The simple summation of multipole moments is fast, but it does not account the penetration energy (Epen). The Epen can be up to 50% of total electrostatic interaction energy (Ees) at the equilibrium distance.

Our concept is taken from the theoretical crystallography. We applied aspherical pseudoatom databank (University at Buffalo DataBank - UBDB) which can easily reproduce the averaged electron density and calculate the Ees. We also tested reproduced electron densities from a new algorithm of refinement procedure, which differs from this commonly used in the databanks. However, the best performance is achieved when the promolecule model of an electron density is augmented by point charges fitted to electrostatic potential (RESP). It enables estimation of the exact electrostatic interaction energy and, by its simplicity, it allows to omit computational-costly integration procedure. Our recent researches show that the RESP charges can be successfully replaced by the point charges from other - easy attainable - sources: from database or from semiempirical methods.

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Keywords: electrostatic interaction energy, penetration effects

MS21-P07

'Pancake' bonding: a charge density perspective

Delia Haynes1

1. Department of Chemistry & Polymer Science, Stellenbosch University, Stellenbosch, South Africa

email: dhaynes@sun.ac.za

A class of thiazyl radicals, 1,2,3,5-dithiadiazolyls (R-CNS-SN', hereafter DTDAs), have been the focus of much investigation due to their potential as building blocks for magnetic and conducting materials. [1] However, these molecules tend to dimerise in the solid state *via* a spin-pairing interaction known as 'pancake bonding' [2], rendering them diamagnetic. Experimental charge density analysis has been carried out on a number of DTDA homodimers, heterodimers and monomers. [3] These data, as well as various computational results, are assessed to probe the nature of the 'pancake bonds' in DTDAs.

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Keywords: dithiadiazolyls, pancake bonding

MS21-P08

Crystal and electronic structure of Ruthenium(II) complex

Julia Koziskova1, Jozef Kožíšek1,

 Institute of Physical Chemistry and Chemical Physics, Slovak University of Technology in Bratislava, Bratislava, Slovakia

email: julia.koziskova@stuba.sk

The crystal structure of Ruthenium(II) complex, $C_{24}H_{26}Cl-N_2O_4Ru\cdot PF_6$, has been determined and analyzed in terms of connectivity and packing patterns. The compound crystal-lizes in the monoclinic crystal system in the space group P_{21}/c , with one cation and one anion in the asymmetric unit [1].

Biological effects of ruthenium complexes and their potential use as metal-based drugs, especially as anticancer agents are one of the leading area. Excluding widespread use of platinum-based chemotherapeutics, ruthenium-based complexes are among the most promising alternatives.

Data collection was performed on a Stoe STADIVARI diffractometer with a Dectris Pilatus 300K detector and with an Incoatec IµS Ag microfocus source (Ag-K α , λ = 0.56083 Å) at 100 K using a nitrogen gas open-flow cooler Cobra from Oxford Cryosystems. Data reduction was processed using X-Area [2]. For numerical absorption corrections a crystal-shape model with 10 faces was employed. An average redundancy of 18.28 gives Rint of 3.18%. A Hirshfeld surface analysis was carried out and two-dimensional (2D) fingerprint plots [3] were generated to visualize the intermolecular interactions and to provide quantitative data for their relative contributions. Direction cosines were applied for the anisotropic secondary extinction correction. The results of multipole refinement were performed on F² using XD suite of programs. After the multipole refinement a topological analysis of the charge density was done. In addition, these results were compared with the electrostatic potential from Hirshfeld surfaces.

Acknowledgement

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Keywords: ruthenium(II) complex, electrostatic potential, charge density

MS22- Molecular structure and chemical properties: chemistry meets charge density

Chairs: Dr. Vladimir Stilinovic, Dr. Jacob Overgaard

MS22-P01

HAR and TAAM eefinements of model crystal structures using CuKa and MoKa X-ray diffraction data

Monika Wanat1-2 Maura Malinska2, Krzysztof Wozniak2

- 1. College of Inter-Faculty Individual Studies in Mathematics and Natural Sciences (MISMaP), University of Warsaw
- 2. Biological and Chemical Research Centre, Chemistry Department, University of Warsaw, Warsaw, Poland

email: mwanat@uw.edu.pl

Commonly, the Independent Atom Model (IAM) of electron density is used in the case of routine X-ray data analysis. However, this model does not give a quantitative description of electron density distribution because atoms are assumed to be neutral and spherical. A far better model that allows for modelling of deformation of spherical charge density was introduced by Hansen and Coppens¹ and is called a pseudoatom model of electron density. Application of this kind of model requires an excellent quality crystals and high resolution XRD data. Quite often, this is difficult to be fulfilled. Therefore, new methods have been developed that enable reconstruction of electron density i.e. Hirshfeld Atom Refinement (HAR)² or Transferable Aspherical Atom Model (TAAM)³.

Validation of application of HAR and TAAM methods for low-resolution data will be presented. For three compounds following refinements of CuKa and MoKa data will be presented: IAM, TAAM (isotropic H atoms), TAAM (using Shade), HAR (isotropic H atoms), HAR (anisotropic H atoms), HAR (using Shade). Additionally, the multipole model and higher order of TAAM and HAR refinements will be presented for MoKa X-ray diffraction data. Analysis of geometry, ADPs (Fig. 1), fractal dimension plots and residual density maps will be shown in comparison with neutron diffraction data.

Fig.1 PEANUT representations of the difference between ADPs obtained from neutron data refinement and HAR, TAAM refinements for MoKa and CuKa data. Root mean square difference scale of 2 was used.



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Keywords: Hirshfeld Atom Refinement, Transferable Aspherical Atom Model, charge density

MS22-P02

Experimental charge density for $\boldsymbol{\sigma}$ hole interactions

Ulli Englert¹, Ruimin Wang², Daniel Hartnick², Shannon Potts², Irmgard Kalf²

- 1. Inorganic Chemistry, RWTH Aachen University, Aachen, Germany
- 2. RWTH Aachen, Aachen, Germany

email: ullrich.englert@ac.rwth-aachen.de

Halogen bonds and σ hole interactions do not only play an important role in crystal engineering but are also relevant for understanding chemical reactivity.

3,3-dimethyl-1-(trifluoromethyl)-1,3-dihydro-1 λ^3 ,2-benziodoxole, 1, commonly known as "Togni reagent" [1], is used for the electrophilic transfer of the trifluoromethyl group by reductive elimination. The σ hole associated with the hypervalent iodine atom is essential for this reactivity. [2] Based on high resolution X-ray diffraction, we have determined the experimental electron density for 1. In the crystal, it interacts with a neighbouring molecule via O…I contacts of 2.9809(6) Å. We compare 1 with two cocrystals 2 and 3 (see Scheme) in terms of electrostatic potential and QTAIM properties in the bond critical point (bcp) for the σ hole interaction. In 2, tetrafluorodiiodobenzene (TFDIB) interacts with two molecules of dimethylaminopyridine (DMAP); the N···I halogen bond is as short as 2.6622(4) Å. With respect to its electronic properties, it resembles a coordinative bond [3]. 3 consists of infinite chains in which diaminobicyclooctane (DABCO) and TFDIB alternate; the N…I contacts are significantly longer but still much shorter than O...I in the case of the Togni reagent. The bcps for the halogen bonds in 3 fall in the range of electron depletion associated with the σ hole on iodine; consequently, the electron density in the bcps is surprisingly small.

In conclusion, the three examples documented in this contribution underline the very wide range of σ hole interactions.



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Keywords: intermolecular interactions, electron density, high resolution.

MS22-P03

Property studies for the heterobimetallic phosphido-bridged W and Mo complexes through charge density analysis

Shin-Guang Shyu¹, Ch-Rung Lee², Wei-Ting Chen³, I-Jui Hsu³

- 1. Institute of Chemistry, Academia Sinica, Taipei, Taiwan
- Department and Institute of Chemical and Materials Engineering, Minghsin University of Science and Technology, HsinChu, Taiwan
- 3. Department of Molecular Science and Engineering, National Taipei University of Technology, Taipei, Taiwan

email: sgshyu@gate.sinica.edu.tw

The chemical bonds and reactions of the (Cp)(CO)2W(m-PPh2)Mo(CO)5 (1) and (Cp)(CO)3W(m-PPh2)Mo(CO)5 (2) complexes were calculated by density functional theory (DFT) method to gain an insight into the property of heterobimetallic metal-metal bond. Based on quantum theory of atoms in molecules (QTAIM), all chemical bonds of optimized geometry will be characterized by bond critical point (BCP) and its associated topological properties, and these results are further compared with single crystal charge density experimental data. Using exchange functional PBE0-D3BJ can provide better calculation results whether it performed through the ZORA approximation of all-electron relativistic method or the pseudopotential method. In complex 1, the characters of the CO on Mo semibridges to W can be confirmed by the BCP between C and W (rc ~ 0.20 e/Å3). Based on fragment charge analysis of DFT calculations, Mo(CO)5 fragment of complex 1 (-0.092) is more positive than that of complex 2 (-0.184), and CpW(-CO)2 fragment of complex 1 (0.208) is more negative than CpW(CO)3 fragment of complex 2 (0.321). These results imply that a dative metal-metal bonding is formed by the electron donation from Mo to W. On the other hand, an intermediate without metal-metal bonding between Mo and W can be formed from complex 1 through semibridging CO transferring from Mo to W, and the transition state of this reaction can be located. This result explains the phenomenon of phosphine addition to Mo cis-site, which is observed in our previous publications.

Keywords: heterobimetallic, metal-metal bond, DFT

MS22-P04

Influence of chosen synthons on the polarizabilities of functional groups

Anna Krawczuk1, Marcin Kaczmarczyk1

1. Faculty of Chemistry, Jagiellonian University in Krakow, Krakow, Poland

email: krawczuk@chemia.uj.edu.pl

The correlation between the crystal structure and physical properties of a given material has long been a subject of many studies. One of the key features of designing efficient multifunctional materials is to use specific building blocks and/or synthons in order to increase a desired effect in the certain crystallographic direction. For example, to obtain efficient optical devices it is necessary to use highly polarizable functional groups which will promote high optical effect. It is thus crucial to get a precise information on how those group polarizabilities are influenced by common synthons used in crystal engineering.

Recently developed routine, PolaBer [1] allows to calculate atomic polarizabilities, and therefore group polarizabilities, based on the definition of atomic dipole moments given by Bader [2]. The routine uses the results of QTAIM partitioning of electron densities. According to QTAIM theory each atomic contribution can be expressed as a sum of atomic polarization and charge translation terms. The numerical derivatives of these quantities with respect to external electric field provide atomic and group polarizabilities. The advantage of using group polarizabilities rather than molecular ones, is the fact that we can extract separate information about the functional group and intermolecular contribution into linear susceptibility. This, on the other hand, enables to identify which group mostly contributes to the global dielectric constant, thus could be very helpful in reverse crystal engineering [3] purpose when designing new optically effective materials.

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Keywords: group polarizability, synthons, optical properties

MS22-P05

Deciphering the driving forces in crystal packings by analysis of electrostatic energies and contact enrichment ratios

Christian Jelsch¹, Yvon Bibila Mayaya Bisseyou²

- 1. CRM2 CNRS Lorraine University, Vandoeuvre les Nancy, France
- 2. Universite Felix Houphouet-Boigny, Abidjan, Cote D'Ivoire

email: christian.jelsch@univ-lorraine.fr

The decomposition of the crystal contact surface between pairs of interacting chemical species enables to derive an enrichment ratio [1,2,3]. This descriptor yields information on the propensity of chemical species to form intermolecular interactions with themselves and other species. The enrichment ratio is obtained by comparing the actual contacts in the crystal with those computed as if all types of contacts had the same probability to form.

The enrichments and contacts tendencies were analysed in several families of compounds, based on chemical composition and aromatic character. As expected, the polar contacts of type H···N, H···O and H···S, which are generally hydrogen bonds, show enrichment values larger than unity.

Hydrophobic contacts show different types of behaviour depending on the molecular content.

The electrostatic energy of short contacts was also computed using charge density models transfered from the EL-MAM2 database.

The contact enrichment ratios were statistically compared with the electrostatic energy values.

The analysis suggests that strong attractive interactions are enriched and are a driving force in the crystal packing formation.

On the other hand repulsive interactions are generally avoided or under-represented.

The behaviour of weaker interactions is less contrasted and will be discussed.

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Keywords: electrostatic , contacts , enrichment

MS22-P06

Molecular thermal smeared electrostatic potential

Christian Hubschle¹, Sander van Smaalen¹

1. University of Bayreuth/Laboratory of Crystallography, Bayreuth, Germany

email: chuebsch@moliso.de

A method to compute the electrostatic potential (ESP) of dynamic-charge-density distributions[1] has been recently reported. Hirshfeld partitioning is a widely used and accepted technique to get individual properties of atoms or molecules in crystals[2]. It is a computationally easy fuzzy partitioning based on simple independent atom model (IAM). We present a way to partition thermal smeared dynamic electron densities. By combining both methods it is possible to get molecular thermal smeared electrostatic potential.

We will present the crystal ESP of dynamic charge densities of α -, γ -boron and boron carbide mapped on Hirshfeld surfaces and molecular ESP of nucleic acid bases. All methods can be easily and quickly applied within MoleCoolQt[3]. In that program it is also possible to export surfaces in file formats suitable for 3D printers.

Figure 1:

Left: Hirshfeld surfaces of Hoogsteen base pair Methyl-Adenine-Methyl-Thymine printed in PLA with magnets on the contact sites.

Right: Hirshfeld of the icosahedral substructure of γ -boron printed in PLA(lower) and mapped by the ESP of dynamic charge densities.(upper)

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Keywords: electrostatic potential, Hirshfeld surface, dynamiccharge-density

MS22-P07

Crystal and electronic structure of 3-(2'-tetrahydropyranyloxy)-4methylthiazole-2(3H)-thione

Jozef Kozisek¹, Julia Koziskova¹, Lukáš Bučinský¹, Peter Herich¹, Jens Hartung², Mike Müller²

- Institute of Physical Chemistry and Chemical Physics, Slovak University of Technology in Bratislava, Bratislava, Slovakia
- 2. Fachbereich Chemie, Organische Chemie, Technische Universität Kaiserslautern, Kaiserslautern, Germany

email: jozef.kozisek@stuba.sk

The title compound is an O-ester structurally deriving from heterocyclic thiohydroxamic acid 3-hydroxy-4-methylthiazole-2(3H)-thione. When heated in the presence of organic peroxides or azo compounds as chemical initiators, the nitrogen-oxygen bonds in 3-alkoxy-4-methylthiazole-2(3H)-thiones breaks homolytically to yield oxygen-centered radicals in unprecedented specificity. Increasing steric demand at oxygen along the sequence primary, secondary, and tertiary alkyl surprisingly shortens the nitrogen oxygen bond in O-alkyl thiohydroxamates pointing to an unknown stabilizing electronic effect induced by steric demand. This responsivity is particularly significant for thiazole-2(3H)-thione-derived cyclic thiohydroxamic acids. In order to correlate N,O-bond lengths to changes in electron distribution the crystal and electronic structure of 3-(2'-tetrahydropyranyloxy)-4-methylthiazole-2(3H)-thione, CoH-13NO₂S₂, has been determined and analyzed in terms of connectivity and packing patterns. The compound crystallizes in the monoclinic crystal system in the space group $P2_1/n$.

Data collection was performed on a Stoe STADIVARI diffractometer with a Dectris Pilatus 300K detector and with an Incoatec IµS Ag microfocus source (Ag-Ka, $\lambda = 0.56083$ Å) at 100 K using a nitrogen gas open-flow cooler Cobra from Oxford Cryosystems. Data reduction was processed using X-Area [1]. For numerical absorption corrections a crystal-shape model with 17 faces was employed. Resolution of 0.37 Å, an average redundancy of 14.29 gives R_{int} of 7.22%. Multipole refinement was performed on F² using XD suite of programs. The preliminary results shows that both N1 and O1 atoms are negatively charged and that the Laplacian has a small positive value. Comparison of experimental and theoretical results will be discussed.

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Keywords: quantum crystallography, IAM analysis, charge density

MS23- Advances in electron crystallography methods

Chairs: Dr. Mariana Klementova, Dr. Enrico Mugaioli

MS23-P01

Continuous rotation electron diffraction: an approach for better understanding of beam sensitive materials

Zhehao Huang1, Xiaodong Zou

 Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden

email: zhehao.huang@mmk.su.se

Nanoporous materials, such as metal-organic frameworks (MOFs) and zeolites are attracting increasing interest because of their particular high performance in catalysis, gas storage, separation, ion exchange, fuel cells, supercapacitor, etc. A crucial problem in the study of porous materials is to determine the structure, more specifically, the atomic positions. The novel properties of nanoporous materials can be revealed by knowing the atomic positions, and then specific applications could be designed. However, MOFs and zeolites are often resulted in nano-size, and high beam sensitivities, which leads to difficulties in structural determination. A newly developed method, continuous rotation electron diffraction (cRED) method, is extended from electron crystallography^[1,2]. Due to the high signal to background ratio and high frame rate of the direct electron detector, we are capable of collecting the dataset in less than one minute. Thus, the major problem in electron diffraction, the beam damage, could be minimized. As a consequence, more details of the beam sensitive materials can be revealed.

cRED method was applied to reveal the structural details of a MOF, PCN-415^[3]. The crystal size of PCN-415 is less than 1 mm, which is too small to be solved by single X-ray diffraction. Ultrafast data collection (17 s – 3 min per dataset) was carried out to minimize beam damage on the MOF. From 3D reciprocal lattice of PCN-415, unit cell and possible space groups were easily determined. The structures were solved and refined by using Shelx software against the *c*RED data. They were further refined against synchrotron PXRD data by Rietveld method. The structure models refined against *c*RED and PXRD show excellent agreement with each other, and the atomic positions differ on average only by 0.032 Å for Zr/Ti and by 0.071 Å for O/C.

Inspecting the structural details, PCN-415 is consisted by a new type of cluster, $[Ti_8Zr_2O_{12}(COO)_{16}]$. Each of them is connected to 16 terephthalic acid (BDC) linkers to form a 3D framework. There is a tetragonal cage with a diameter of 9 Å and an octahedral cage with a diameter of 11 Å. Two types of symmetrically independent BDC linkers are observed. Topologically, a pair of parallel BDC linkers within the equatorial plane is regarded as one edge. Therefore, eight equatorial BDC linkers are simplified into four edges. On the other hand, eight BDC linkers above and below the equatorial plane are simplified into eight edges. As a result, the $[Ti_8Zr_2O_{12}(COO)_{16}]$ cluster acts as a 12-connected node, affording a network with **fcu** topology. Because of the new cluster, PCN-415 has outstanding photoactive property. The optical band gap was calculated to be 3.3 eV based on the UV-Vis spectrum, and can be further turned by amine-functionalization of BDC linkers. In combination with the high porosity (BET surface area of 1050 m²·g⁻¹), and excellent chemical stability (in pH range of 0–13), PCN-415 provides ideal platforms for the design of MOF photocatalysts. Among all the tested materials, amine-functionalized PCN-415-NH₂ shows the highest activity with an H₂ evolution rate of 594 µmol g⁻¹ h⁻¹. These results highlight the effect of new clusters in PCN-415 as photoactive species for photochemical hydrogen production as well as *c*RED method as a powerful tool for the structural study of beam sensitive materials.



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Keywords: electron crystallography, metal-organic framework, beam sensitive materials

Towards automated data collection for continuous rotation electron diffraction: current status and development

Bin Wang1, Stef Smeets1, Hongyi Xu 1, Xiaodong Zou1

 Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden

email: bin.wang@mmk.su.se

Electron diffraction tomography has been developing during the past 10 years and is proven to be very helpful in crystal structure determination [1], especially for beam sensitive materials such as zeolites, metal-organic frameworks (MOFs), and even proteins. The development of data collection methods went from discrete sampling of the reciprocal space (ADT, RED, etc.) to continuous data collection [2] with the help of fast electron counting detectors. Structure solution usually requires high tilt range and minimal dynamical effects from electrons, while for beam sensitive materials it is also desired to have minimum beam damage to the sample. The conventional discrete sampling methods suffer in this case from higher beam damage because of longer electron exposure time. The continuous method is thus preferable because it not only reduces data collection time, but also integrates the reflection intensities over the exposure time interval, which improves the accuracy of intensity extraction. However, the method is highly limited by the mechanical instabilities of goniometers inside the transmission electron microscopes (TEM) that the crystals can easily move out of the beam during data collection.

Here we illustrate the current status of the continuous rotation electron diffraction (cRED) method by showing that refinement against only electron diffraction data has been feasible. Datasets with high tilt ranges (i.e. > 100°) were collected for a MOF sample, Co-CAU-36, on different crystals and initial structure solution for the datasets from SIR2014 showed clearly the existence of the porphyrins and even guest molecules in the pores. By comparing refinement results from different individual datasets, the deviation for framework atoms was on average 0.04 Å, while for atoms in the guest molecules the deviation was on average 0.11 Å. Furthermore, the whole process from TEM sample preparation to the refined structure took only 9 hours.

However, collection of high quality cRED data still requires reasonable experience, i.e. blindly tracking back the crystal which might be moving out of the beam is not very straightforward. With development of electron diffraction data collection softwares such as Instamatic [3], automatic tracking back of the crystals becomes feasible by taking a defocused diffraction image regularly, performing cross correlation for how much the crystal has moved, and apply lens change to make the beam chase the crystal. In the cost of losing around 10% of diffraction data, higher tilt range can be achieved in a fully automated manner. This allows a normal electron diffraction experimentalist to collect datasets with higher tilt ranges. Further development is still needed and we aim to build up a fully automatic cRED data collection protocol, with automated crystal finding and continuous rotation data collection.

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Keywords: Continuous rotation electron diffraction, method development, automation

Structure determination by ultra-fast electron diffraction of the new zeolite ITQ-62

Jose Luis Jorda Moret¹, Pablo J. Bereciartua¹, Lindiane Bieseki¹, Raquel Simancas¹, Jorge Simancas¹, Fernando Rey¹, Avelino Corma¹, Susana Valencia¹, Sibele B. Pergher²

- Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas, Valencia, Spain
- 2. Universidade Federal do Rio Grande do Norte, Natal, Brazil

email: jjorda@itq.upv.es

Zeolites are crystalline microporous silica-based materials. In many cases, the isomorphic incorporation of heteroatoms replacing silicon confers the resulting materials interesting catalytic properties which can be tailored for a particular catalytic reaction. So, the properties and applications of zeolites depend on their chemical composition as well as on the size and spatial distribution of their channel systems.

During the synthesis of the novel zeolite ITQ-55 [1], variations of the synthesis conditions lead to the formation of an additional new zeolite, called ITQ-62 [2]. ITQ-62 proved to be stable after removing the organic structure directing agent. The laboratory PXRD pattern was indexed using the program TREOR in an orthorhombic unit cell with a=21.068 Å, b=17.254 Å and c=7.554 Å, while the systematic extinctions suggested as the most probable extinction symbol C – –, corresponding to space groups C222, C2mm, Cm2m, Cm2m or Cmmm.

The structure determination was attempted by two independent methods.

In the first method one sample of ITQ-62 was calcined at 923 K, transferred to a glass capillary and sealed. The XRPD pattern was measured at beamline MSPD of the Spanish Synchrotron Light Source ALBA using a high resolution setup. The integrated intensities were extracted using the program FULLPROF, and the crystal structure was solved using the program FOCUS, obtaining a reasonable structure.

In the second method, the non-calcined sample, still containing the organic structure directing agent, was measured by ultra-fast electron diffraction tomography (EDT) in a JEOL 2100F microscope operating at 200 kV and using a GATAN Orius SC600A CCD camera. A NanoMEGAS-Digistar P1000 device, attached to the microscope, is also employed to control the precession of the electron beam in order to mimbnimize dynamical scattering effects. This method, recently described, allows collecting large sets of electron diffraction tomography data in just half a minute. [1], [3] Performing the data collection in such a short time allows obtaining good data even for highly beam-sensitive samples, as the measurement is completed before the beam damage destroys the crystalline structure. The crystal structure was solved again with FOCUS, obtaining an identical solution.

Finally, the structure was validated by a Rietveld refinement of the XRPD data using FULLPROF, showing a good agreement between the experimental data and the refined structure. In conclusion, ultra-fast EDT has been proved to be an extremely useful tool for the structure solution of materials, even if they exhibit a low stability to the electron beam.



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Keywords: Electron, crystallography, zeolite

TEM-based analysis of the crystal structure of a Ge-rich layer sandwiched between spintronic Fe₃Si

Holm Kirmse¹, Bernd Jenichen², Elena Willinger³, Xing Huang³, Benedikt Haas¹, Christoph T. Koch¹

- 1. Humboldt University of Berlin, Dept. of Physics, Structure
- Physics and Electron Microscopy Group, Berlin, Germany
- 2. Paul Drude Institute, Berlin, Germany
- 3. Fritz Haber Institute, Berlin, Germany

email: holm.kirmse@physik.hu-berlin.de

Introduction

The magnetic properties of Fe₃Si make it an excellent candidate for spintronic applications [1]. For a switchable device, two layers of Fe₃Si have to be separated by a thin semiconducting interlayer. Ge was chosen for this interlayer having a nominal thickness of 3 nm only. Sharp interfaces were ensured by solid phase epitaxy [2] which is a two-step approach comprising of layer deposition at 150 °C and recrystallization at 300 °C. From bulk crystals Fm3m space group is expected for Fe₃Si and Fd3m for Ge [3].

Objectives

This work aims at both, crystal structure and composition analysis of the layer stack by transmission electron microscopy (TEM)-based techniques. In particular, nano-beam diffraction (NBD), high-angle annular dark-field atomic-resolution scanning TEM (HAADF ARSTEM) imaging and energy dispersive X-ray spectroscopy (EDXS) were applied for full crystallographic phase analysis.

Results

The generated crystallographic phase of Fe₃Si perfectly corresponds to both, the expected crystal structure and the chemical composition. In contrast to that, superstructure reflections along [001] are observed for the nominal Ge layer. This hints to an ordering along [001]. Moreover, EDXS revealed a composition ratio of about 6:3:1 for Ge:Fe:Si. Both results point to an unexpected crystallographic phase of the interlayer. For gaining real space information, HAADF AR-STEM imaging was performed along [100] and [110] direction (see Fig. 1, center and right image, correspondingly). Bright spots correspond to atomic columns. The brightness depends on the mean atomic number of the individual column. Both projections consistently reveal ordering along [001]. Brighter spots are dedicated to Ge and weaker spots to Fe columns. Filled interlayers exhibit a larger distance along [001] of z = 0.52 compared to z = 0.48 for the empty layers.

Conclusion

The semiconductor interlayer is composed of P4mm Ge₂Fe (see Fig. 1 left). The deviation of the position of the atomic columns from the ideal positions at 0.50 and 0.75 is most likely due to the relaxation of strain introduced by the ordering.



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Keywords: TEM, Spintronics, Ge₂Fe on Fe₃Si

Possibility of Improved Phasing Method for MicroED – experimental aspects

Cathal Cassidy1, Tsumoru Shintake

1. Okinawa Institute of Science & Technology, Onna, Japan

email: c.cassidy@oist.jp

The authors introduce some experimental data in support of a potential new way of capturing diffraction in a transmission electron microscope. There is a possibility to improve the phasing process in protein crystallography (Micro-ED) with this approach. To date, we have acquired several diffraction data sets from MgO nanocubes (as a test specimen), along with supporting conventional HRTEM and far-field diffraction data, for reference purposes. Data has been acquired in an FEI Titan microscope, operated at 300kV, as well as in a JEOL ARM-200F microscope, operated at 200kV. We have also acquired preliminary data on carbamazepine and lysozyme nanocrystals.

Keywords: electron diffraction, nanocrystal, phasing

MS23-P06

Low-dose electron diffraction tomography

Holger Klein1, Stéphanie Kodjikian1

1. Institut Néel, Univ. Grenoble Alpes and CNRS, Grenoble, France

email: holger.klein@neel.cnrs.fr

New materials are invented every day, to respond to ever more complex societal and economic issues (pharmaceuticals, soil decontamination, energy conversion etc. ...). The understanding and development of these materials goes inevitably through a stage of structures determination. In the research on nanomaterials, transmission electron microscopy is proving to be a particularly suitable technique, since it exploits the property of electrons to interact strongly with matter - an extraordinary advantage for studying nano-sized materials.

However, important classes of materials like metal-organic frameworks (MOFs), zeolites and biological crystals are sensitive to the electron beam. Classical investigation techniques that necessitate a too high electron dose for the acquisition of the data then become powerless. New experimental methods are needed.

We present here an innovative method to study the atomic structure of sensitive materials by electron diffraction. Our method opens the field of application of electron crystallography to beam sensitive materials, such as MOFs and biological crystals. It requires only a standard TEM, without any particular equipment, except for a fast camera with a high sensitivity and a beam precession system.

Each aspect of low-dose electron diffraction tomography has been optimized to limit the total irradiation time of the sample: no preliminary crystalline orientation is necessary and the beam is systematically blanked between two successive exposures. Thus the crystal is irradiated only during the acquisition of diffraction patterns, i.e. only when the irradiation is useful in terms of diffraction.

The quality of the recorded data was tested by the resolution of two complex structures: $Sr_5CuGe_9O_{24}$ and manganese formiate $[Mn(HCOO)_2(H_2O)_2]_{ex}$ the latter of which is beam sensitive. Both structures are obtained with great precision. We evaluated the number of frames needed to obtain reliable structural models.

Low-dose electron diffraction tomography has three main advantages:

- It provides a set of data suitable for structural resolution with an extremely low cumulative electron dose of 0.27 e⁻/Å², ten times less than the dose usually used in cryo-TEM structural determinations.
- Because of its speed and the simplicity of its implementation, it can be used routinely for the study of a great number of particles in a powder sample.
- It only requires equipment that is standard in a large number of laboratories.



Keywords: low dose, electron diffraction tomography, structure solution

Applications of the highly efficient lowdose electron diffraction tomography

Stéphanie Kodjikian1, Holger Klein1

1. Institut Néel, CNRS and Université Grenoble-Alpes, Grenoble, France

email: stephanie.kodjikian@neel.cnrs.fr

The understanding of the properties of a material comes from the knowledge of its structure. This is true for all materials, and beam sensitive materials don't escape from this rule. However, not only the complex structure of the latter is an issue, but also the difficulty of obtaining sufficient and reliable data before the sample is destroyed by the beam. With this in mind we have developed a new and highly efficient method of electron diffraction data acquisition: lowdose electron diffraction tomography (LD-EDT) that we apply here to two different materials.

A first test of the performance of this method was the solution of the complex monoclinic oxide $Sr_5CuGe_9O_{24}$ from a data set of 100 frames. PETS and Superflip in JANA2006 yielded a structural model containing all 22 independent atom positions. A comparison with the X-ray refined structure shows the high precision of our solution.

The successful application of the LD-EDT to beam sensitive materials depends on its efficient use of the electron dose. The total dose depends on the exposure time for each frame and the number of frames in the data set. As the completeness and the redundancy of the data have been shown to be decisive parameters in electron crystallography, a large number of recorded frames is an asset for the structure solution, while each additional frame adds some dose to the crystal.

We have therefore tested the influence of the number of LD-EDT frames in the data set on the structure solutions. The complete data set was reduced by using only 50, 40, 30 or 20 frames in the structure solution procedure. Even though the data set completeness and redundancy are much lower than what is usually necessary for precise structure solutions, they are sufficient when the data is acquired by LD-EDT. One reason for the tolerance towards smaller data sets might be the higher data quality due to the fact that the beam is larger than the sample and therefore the diffracting volume is the same for each frame during the acquisition.

Very short exposure times of the individual frames are also sufficient for the data acquisition. As an example the structure of a beam sensitive metal-organic framework (MOF), manganese formiate [Mn(HCOO)₂(H₂O)₂]_{...} has been solved. Exposure times of 0.2 s in a very weak beam (total dose of 0.27 $e'/Å^2$) yielded the complete structure to a high degree of precision.



Keywords: Low dose, Electron diffraction tomography, Structure solution

First preliminary results from TAAM-UBDB refinement on electron diffraction data

Paulina Dominiak¹, Michał Chodkiewicz¹, Joanna Krzeszczakowska¹

 Biological and Chemical Research Centre, Department of Chemistry, University of Warsaw, Warszawa, Poland

email: pdomin@chem.uw.edu.pl

Cryo-electron microscopy and electron diffraction methods have made enormous progress in the last years and an increasing number of atomic and near atomic resolution structures are becoming available. At present, interpretation of collected data relay on a very approximate scattering model. The model is based on spherical independent atoms (IAM), ignoring the charge redistribution due to chemical bonding. This approximation may lead to unnecessary loss of information. We propose to base interpretation of data from cryo-electron microscopy and from electron diffraction methods on more realistic electron scattering models.

We are developing Transferable Aspherical Atom Models (TAAMs) from detailed electron densities of molecules and crystals. To build TAAMs we use a databank of aspherical atomic electron densities called UBDB [1]. Currently UBDB allow to reconstruct electron density of any protein, nucleic acid or other biologically important molecule. Thus, it gives also fast access to electrostatic potential.

It has been shown already [2] that replacement of the IAM by TAAM in x-ray crystallography leads to more accurate geometrical information and provide access to quantitative estimation of the electron density distribution and properties derived from it for molecules in a crystalline environment.

Given the fact that electron diffraction is more sensitive to charge density redistribution than x-ray we expect to see even more pronounced improvement after introduction of TAAM to analysis of electron diffraction/scattering.

We will present our first preliminary results of TA-AM-UBDB refinements against electron diffraction data collected for paracetamol[3]. The figure illustrates the difference in crystal electrostatic potential (e/bohr) resulting from the differences between the IAM and the TA-AM-UBDB electron scattering models.



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Keywords: electron crystallography, UBDB, electrostatic potential modelling

MS23-P09

Riding the camel: the double-peaked rocking curve and its use in the processing of precession electron diffraction data

Lukáš Palatinus1, Petr Brázda1

1. Department of Structure Analysis, Institute of Physics of the CAS, Prague, Czech Republic

email: palat@fzu.cz

Data collected by the precession electron diffraction (PED) technique can be successfully used for solution and also accurate refinement of unknown crystal structures. Especially efficient in this respect is the technique of PED tomography (PEDT), where a series of PED patterns are collected on a crystal progressively tilted by small steps around a rotation axis [1].

Such PEDT data have certain special characteristics that make it different from standard rotation data. The most prominent is the rocking curve of a reflection in PEDT data, i.e. the reflection intensity as a function of the tilt angle. While the rocking curve of non-precession data is a narrow single peaked function, the rocking curve of a reflection in PED is a broad function with two maxima. Typically, each reflection is measured several times. The precession angle is usually much larger than the angular width of the non-precession rocking curve of the reflections, and therefore the width and shape of the rocking curve is determined mostly by the precession angle and not so much by the crystal itself. Because of the specific shape of the curve, we call the plot of the precession rocking rocking curve colloquially "the camel plot".

This feature can be exploited in several way during the analysis of the PEDT data. One of the applications is the refinement of the crystal orientation. The crystals are often not steady during the PEDT experiment, but they turn. Ignoring this rotation leads to distorted data sets and very inaccurate lattice parameters. Using the knowledge of the rocking curve shape allows an accurate refinement of the crystal orientation during the experiment and substantial improvement of the data.

The knowledge of the rocking curve can also be exploited in the intensity extraction. The typical approach to the determination of the total intensity of certain reflection is the integration of intensity accross all frames on which the reflection is measured. However, this provides inaccurate results for partially covered reflections and it is also sensitive to intensity variations due to dynamical diffraction. Knowng the rocking curve allows the total intensity to be determined more accurately by fitting the rocking curve profile to the reflection intesities.

Implementation of these features in the computer program PETS 2.0 [2] and their application to a number of practical examples shows that "riding the camel" can lead to significantly improved data quality and sometimes make a difference between a solved and unsolved structure.

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Keywords: precession electron diffraction, intensity extraction,

Electron crystallography greatly expands organic and inorganic X-ray crystal structure determination

Tim Gruene1

 Energy and Environment Research Division, Paul Scherrer Institut, Villigen PSI, Switzerland

email: tim.gruene@psi.ch

X-ray crystallography is the main discipline in chemistry that provides the 3D coordinates of molecules. The crystal structure is an essential aspect in many fields in chemistry. Electrons offer a fascinating extension to X-rays. Crystals smaller than the grains in icing sugar can be investigated too small for X-rays. 3D single crystal structures can be determinaed from powder, including caseswhere crystal size affects the chemistry, like for catalysts and MOFs[1].

This application of electron crystallography (EC) is young and was made possible with the adaption of the rotation method to[2]. Many publications proof the reliability of the coordinates from EC. Despite all these advantages, EC only plays a niche role in structural chemistry: it accounts for much less than 1% of all published 3D single crystal. This is in stark contrast to the number of crystalline powders, that, like in the case of Novartis, exceeds the number of available single crystals by a factor of 3-4.

One of the main reasons for this discrepancy could be the difference in methods and software that are available to process and refine EC data. The combination of PEDT and Jana2006 can improve the model R1-factor down to X-ray levels, and produce the hydrogen atoms in a heavy atom structure with striking clarity[3]. However, this level of accuracy is not required for the average crystal structure. In this presentation I report on our success to copy X-ray crystallography onto EC. We mounted an EIGER X 1M hybrid pixel detector from Dectris Ltd. to an electron microscope, collected data like with an inhouse X-ray machine and used the methods many structural chemist are well familiar with. We solved the structure of a new organic methylene blue derivative with a unit cell volume of 9,000A3. From 17 fragments of a long needle-like crystal we collected 60 degree wedges and processed all data sets within a few hours. The structure solved with direct methods with default options. The data are accurate enough to complete the model and even model a disordered BF4- solvent molecule. We believe it is time to strongly advertise EC in all its flavours to the Structural Chemistry community.



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Keywords: (in)organic structural chemistry, electron crystallography

MS23-P11

Pushing the limits of material characterization using transmission electron microscopy at the university of oviedo

Zakariae Amghouz
!, Alaa Adawy², José R. García³, Santiago García
-Granda 4

- Department of Materials Science and Metallurgical Engineering, University of Oviedo, Campus Universitario, 33203 Gijón, Spain
- Laboratory of High-Resolution Transmission Electron Microscopy, Scientific and Technical Services, University of Oviedo-CINN, Oviedo, Spain
- 3. Department of Organic and Inorganic Chemistry, University of Oviedo-CINN, Oviedo, Spain
- 4. Department of Physical and Analytical Chemistry, Oviedo, Spain

email: amghouzzakariae@uniovi.es

Electron microscopy is at the forefront of many characterization methodologies used nowadays to obtain valuable structural information for different types of materials down to the atomic scale. In particular, our facility JEOL JEM-2100F provides a platform for combining different characterization techniques, such as high-resolution transmission electron microscopy (HR-TEM); electron diffraction techniques (selected area electron diffraction: SAED, nano-beam electron diffraction: NBD and 3D precession electron diffraction tomography); scanning transmission electron microscopy (STEM) in both bright-field (BF) and high-angle annular dark-field (HAADF) modes; energy dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS). In this communication, we shade the light on outstanding examples that show the beauty of using our facility to effectively characterize inorganic, hybrid inorganic-organic, and biological samples.

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Keywords: HR-TEM, Electron diffraction, EDX

MS24- Defects and disorder quantification at the nanoscale

Chairs: Dr. Partha Pratim Das, Dr. Tatiana Gorelik

MS24-P01

Diffraction effects of powder nano-scale materials

Dmitriy Yatsenko1, Sergey. Tsybulya1

 Novosibirsk State University, Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

email: yatsenko@catalysis.ru

Properties of nanomaterials are defined by features of the atomic structure and morphology. Investigation of crystal structure and nanostructure of such small objects is an actual problem. X-ray diffraction method can be used for this purpose. Anisotropic broadening of the diffraction peaks, redistribution of the intensities or appearance of diffuse scattering can appear for nanomaterials. Standard X-ray diffraction techniques used for bulk materials with periodic structures are often not applicable in this case.

These tasks can be solved by the Debye Function Analysis (DFA) method [1], based on Debye scattering equation (DSE) [2]. It is full-profile method which is applicable for any an arbitrary atoms collection, and therefore can be used for crystalline objects, non-crystalline materials or nanostructures.

Possibilities of modelling diffraction patterns by the DFA by our software [3] will be shown for specific examples of various nanocrystalline materials: hydroxides of magnesium and tungsten, layered structures, metastable forms of aluminum oxide, ultradispersed iron oxides et al. [4]. It is public-domain software available on the website: www. sourceforge.net/projects/dianna.

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Keywords: Nanomaterials, X-ray diffraction, Debye scattering equation.

MS24-P02

Analysis of chemical short range order using single crystal diffuse scattering

Ella Mara Schmidt¹, Reinhard B Neder¹

1. Institute for Crystallography and Structural Physics, FAU Erlangen-Nürnberg, Erlangen, Germany

email: ella.schmidt@fau.de

In the average structure refinement of molecular materials, split positions are often encountered. As a consequence a molecule on one site can be present in more than one orientation. The typical structure refinement stops there and does not consider diffuse scattering, which allows statements about short range order interactions. Building and refining a short range order model to analyze the diffuse scattering takes the structure refinement to the next level.

A complex molecular crystal will usually consist of several components on several sites within the unit cell. Furthermore, a single site may be occupied by molecules in different orientations e.g. a first molecule in orientations A and B on site 1 and a second molecule in orientations C and D on site 2, see Fig. 1. In such systems short range order is common: On a local scale, the molecules tend to show preferred pair-wise arrangements. Characterizing this local order enables profound statements about molecular interactions [1].

With the help of molecular form factors [1] and the theory of diffuse scattering (e.g. Warren [2]), we developed a method that characterizes correlated chemical short range occupational disorder directly in reciprocal space. The diffuse scattering IDiff can be expressed as a function of the indices $h_i k_i l$ in reciprocal space:

 $I_{BB}(h,k,l)=I_{Lase}(h,k,l)+I_{SBO}(h,k,l)$

Where ILaue is the Laue scattering

 $\left(I_{\text{cons}}(h, \mathbf{i}, t) = \sum_{i=1}^{n} \sum_{k=1}^{n} \sum_{j=1}^{n} |\mathbf{F}_{i_i} - \mathbf{F}_{j_i}|^2 \right)$

and I_{SRO} is the short range order scattering:

 $I_{300}(b,k,l) \times \sum_{i,v,v,v} \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} \sum_{m=1}^{n} m_{k} m_{k} F_{k} F_{k}^{*} a_{\mu\nu}^{A,0} \exp(2\pi i (h \cdot u + k \cdot v + l \cdot w))$

Here (u, v, w) are vectors in direct space, n_s is the number of different sites and k_i is the number of possible components on site *i*. m_{A_i} is the concentration of component A on site *i*, f_{A_i} is the molecular form factor of the molecule type A on site *i*. $m_{A_i}^{A_i}$ are the Warren-Cowley short range order parameters, that encode the probability to find an AB pair separated by vector (u, v, w). All parameters, except the $m_{A_i}^{A_i}$ can directly be determined from the average structure refinement.

We apply this formula for the analysis of the diffuse scattering of 9-Bromo-10-Methylanthracene [3]. The model for the short range order can be developed directly in reciprocal space and the formula can be used to perform a least squares regression analysis to fit the short range order parameters quantitatively.

Our method to characterize complex molecular disorder using single crystal diffuse scattering is a powerful tool to understand and model molecular interactions in disordered crystals. As the method treats data directly in reciprocal space and enables least squares fitting of disorder models, calculations can be performed on desktop computers without the excessive use of computation time.

Figure 1:

(a) Refined average unit cell with overlayed components A and B on site 1 and 2.

- (b) Possible configuration of disordered unit cells.
- (c) Diffuse scattering of 9-Bromo-10-Methylanthracene in the 0kl-layer.



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Keywords: diffuse scattering, disorder, single crystal

MS24-P03

NanoMAX Beamline, a nanoprobe beamline for scattering and imaging at MAX IV

Angel Rodriguez Fernandez¹, Ulf Johansson¹, Gerardina Carbone¹, Alexander Björling¹, Sebastian Kalbfleisch¹, Tomas Stankevic¹, Björn Bring¹, Anders Mikkelsen², Ulrich Vogt³

- 1. MAX IV LABORATORY, Lund University, Lund, Sweden
- 2. Synchrotron Radiation Research, Department of Physics, Lund University, Lund, Sweden
- Biomedical & X-Ray Physics, Dept. of Appl. Physics, KTH Royal Inst. of Tech, Stockholm, Sweden

email: angel.rodriguez_fernandez@maxiv.lu.se

NanoMAX is a hard X-ray nanoprobe beamline at the 3 GeV multi-bend achromat storage ring MAX IV, Lund, Sweden [1]. The beamline is designed to utilize the uniquely high brilliance of the facility to achieve nanometer-sized coherent foci with high photon intensity. The small focus is used for scanning imaging with the main methods nano-diffraction, phase and absorption contrast, coherent diffractive imaging and ptychography - in forward and Bragg condition. The beamline optics has been briefly presented earlier [2].

The beamline will have two experimental stations when the buildup phase ends 2019/2020. One experimental station using Kirkpatrick-Baez mirror optics (KB) for focusing. The KB system gives a diffraction limited probe of 40 nm (24 keV) - 200 nm (5 keV) with 100 mm working distance from optics to sample position. The generous space will allow for versatile sample environments. Three main detectors are planned for or installed at the station; a megapixel photon counting area detector in forward direction, a compact photon counting area detector in off-axis position on a commercial industry robot and a 3-element Germanium X-ray fluorescence detector. A compact two axis high precision goniometer will allow advanced studies of ordered samples with diffractive methods. Continuous sample scanning is implemented in a basic version and will be further developed for efficient data acquisition. The design of the second experimental station is ongoing and first tests are anticipated early 2019.

We have provided beamtime to a handful user experiments during the first year of operation. Experiments in X-ray fluorescence, wide-angle scattering, nano-diffraction and ptychography have been executed. To achieve optimal performance from the super-polished KB-mirrors we have developed a simple procedure to measure focus astigmatism by scanning a Siemens star like test structure in ptychographic mode. The test sample image and the probe are reconstructed at the sample position using diffraction data from an inline pixel detector [3]. The probe is then propagated along the beam direction to show the beam profile, in vertical and horizontal plane, as seen in figure 1 bottom parts.



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Keywords: Nanofocus, Hard X-ray, diffraction

MS24-P04

Correlated disorder in a metal-organic framework

Emily Reynolds¹, Mia Baise², Alistair Overy¹, Arkadiy Simonov³, Jamie Gould⁴, Ben Slater², Andrew Goodwin¹

- 1. University of Oxford, Oxford, United Kingdom
- 2. University College London, London, United Kingdom
- 3. University of Freiburg, Freiburg, Germany
- 4. University of Leeds, Leeds, United Kingdom

email: emily.reynolds@chem.ox.ac.uk

At the heart of creating and developing functional materials is understanding structure - a task often complicated by disorder, be it compositional or orientational, static or dynamic. Whilst diffraction techniques have become adept at describing periodicity and understanding atomic structure, deviation from perfect order occurs in most real materials. Traditional crystallographic techniques fail to describe such deviations from periodicity, and while we understand the importance of disorder we are yet to understand how to describe, characterize and control disordered states.

A very specific disordered state is correlated disorder. This state arises when dominant interactions - i.e. chemical bonding - dictate fixed local atomic arrangements that need not result in long-range 3D order but may result in aspects of the structure being correlated. These correlations can produce signature patterns in the measured diffraction pattern in the form of diffuse scattering. In a class of materials known as metal-organic frameworks (MOFs), the local interactions driving formation usually result in long-range periodic arrangements. However, we can introduce disorder in MOFs through asymmetry in the linker, which acts in an analogous way to cyanide in transition-metal cyanides,[1] second-order Jahn-Teller displacements in BaTiO₃ [2] and hydrogen bonding in square ice.[3]

We substitute terephthalate linkers with asymmetric pyrazole-carboxylate and show that while powder and single crystal diffraction data suggest the linkers are disordered, the highly structured diffuse scattering visible in single-crystal X-ray patterns indicates correlated disorder along the linker rows. By comparing experiment with models calculated using simple local rules, we are able to understand the specific type of correlated disorder in a MOF-5 analogue. The fixed local arrangements in the structure results in specific pore chemistry and binding sites important for adsorption and catalytic applications. More generally, these results contribute to the ability to identify specific types of correlated disorder within analogous systems, and therefore a greater understanding of structure on the nanoscale.

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Keywords: Disorder, framework, diffraction

MS24-P05

Structural and optical characteristics of non-polar ZnO epitaxial films grown by radio-frequency magnetron sputtering

Chia-Hung Hsu1, Bi-Hsuan Lin2, Wei-Rein Liu1, Wen-Feng Hsieh3

- 1. Scientific Research Division, National Synchrotron Radiation Research Center, Hsinchu, Taiwan
- 2. Experimental Facility Division, National Synchrotron Radiation Research Center, Hsinchu, Taiwan
- 3. Department of Photonics and Institute of Electro-Optical Engineering, National Chiao Tung University, Hsinchu, Taiwan

email: chsu@nsrrc.org.tw

ZnO is recognized as an important wide band gap semiconductor material for its applications in UV and blue spectral range devices such as light emitting diodes (LEDs), laser diodes (LDs), and photodetectors. The non-centrosymmetric characteristics of its wurtzite structure gives rise to piezoelectric and spontaneous polarizations along the c-axis. The polarization across the interface of c-axis oriented quantum well structures results in the undesired effects such as quantum confined Stark effect and deteriorates the electronic and optical properties of devices. Therefore, many efforts have been put to grow and to characterize non-polar ZnO epitaxial films.

High-quality non-polar a-plane and m-plane ZnO epitaxial films were grown on r-plane and m-plane sapphire substrates, respectively, by radio-frequency magnetron sputtering. The structural characteristics, including strain and structural defects, of both non-polar ZnO films were studied by X-ray diffraction and transmission electron microscopy (TEM). Surface morphology and roughness of the ZnO samples was investigated by atomic force microscopy (AFM). The anisotropic optical properties of the non-polar ZnO films characterized by polarization-dependent photoluminescence (PL) are correlated with its structural features. References:

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Keywords: non-polar ZnO, strain, structural defects

MS25- Combined approaches for the structure determination of new materials at the nanoscale

MS25-P01

Structure of the conducting PANI/CSA polymer system as seen by XRD, neutron diffraction and advanced computer modeling

Wojciech Łużny1, Maciej Śniechowski1, Tomasz Kozik2

- 1. AGH UST, Fac. of Physics and Applied Computer Science, Krakow, Poland
- 2. Department of Photonics and Institute of Electro-Optical Engineering, National Chiao Tung University, Hsinchu, Taiwan AGH UST, Fac. of Physics and Applied Computer Science, Krakow, Poland)

email: luzny@agh.edu.pl

The structure of the conducting polymer system of polyaniline (PANI) protonated with camphorsulfonic acid (CSA) remained unclear for several years and resisted attempts at solving by use of typical methods. This case may serve as an example of how different experimental and computational methods may impact each other and develop a successful, combined approach to structural study aimed at determining a reliable model and verifying its properties.

Molecular dynamics simulations may provide useful information concerning the studied system, even if the accuracy of such simulations is finite. These were performed for PANI/CSA [1] and allowed drawing important conclusions regarding the type of structure - alternating double layers of polymer chains and counterions. Additionally, they suggested the indexing of principle peaks observed in the X-ray powder diffraction pattern obtained for samples of this polymer. Finally, they were the basis for formulating a hypothesis regarding the preferred orientation of crystallites in thin film samples of this system cast from different solvents in agreement with grazing incident beam X-ray diffraction data.

The above described simulations were the foundation for the scope a crystallographic unit cell model. After taking advantage of artificial intelligence based methods aimed at optimizing the layout of the structural units of PANI/CSA within such a cell with respect to the powder diffraction pattern, a new model was found [2]. Apart from satisfying the optimization criteria, is allows explaining the differences observed in neutron diffraction patterns recorded for regular and partially deuterated samples of the studied system. It also has all the previously reported advantages of the principal structure obtained from molecular dynamics simulations and allows verifying the hypothesis regarding preferred orientation in thin films cast from different solvents.

Taking a generalized look at the process of obtaining this new structural model of PANI/CSA, it could be described as an example of a systematic approach in which various
experimental (XRD, grazing incident beam X-ray scattering, neutron diffraction) and computational (molecular dynamics, artificial intelligence) techniques mutually inspirone another and allow developing and verifying a structural model of a polymer system. Each of the contributing pieces listed above by themselves are not enough to develop a good structural model, while combining insight into the studied problem provided by each of them leads to one which is reliable.

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Keywords: polyaniline, crystalline structure, simulations

MS25-P02

Combination of GIWAXS and TEM study in understanding polymer-fullerene fibrillar network structure

Chin-Ti Chen1, Song-Fu Liao2, Chi-Yang Chao2

- 1. Institute of Chemistry + Academia Sinica, Taipei, Taiwan
- 2. Department of Materials Science and Engineering + National Taiwan University, Taipei, Taiwan

email: chintchen@gate.sinica.edu.tw

In addition to the larger absorption coefficient and longer absorption wavelength, high short-circuit current density can be associated to the high portion of face-on, in-plane crystallite orientation of P4TIF, which is evident by GI-WAXS study. GIWAXS study reveals that the face-on (in plane) orientation is most pronounced, lamellar structure, (100), pi-pi stacking structure, (010), and crystallite correlation length are more significant or longer than those of P4TIN. Moreover, thin film morphology probed by TEM reveals the fibril network nanostructure, which is more pronounced in PC61BM-blended P4TIF thin films than P4TIN ones. The chemical structure difference between P4TIF and P4TIN is the fluorine (F) and nitrile (CN) substituent. Such difference in fibrillary morphology, which is in turn due to the different molecular interaction of F or CN, promotes the photocurrent output and hence short-circuit current density of the polymer-based organic photovoltaics.



Keywords: GIWAXS, TEM, polymer-fullerene fibril

MS25-P03

X-ray Absorption spectroscopy options for crystallographic research at BESSY II

Daniel Többens¹, Götz Schuck¹, Ivo Zizak¹, Susan Schorr¹

 Department Structure and Dynamics of Energy Materials, Helmholtz-Zentrum Berlin f
ür Materialien und Energie (HZB), Berlin, Germany

email: daniel.toebbens@helmholtz-berlin.de

X-ray absorption spectroscopy (XAS) is increasingly used to study crystallographic problems in a wide range of scientific fields. Its element specificity and sensitivity to the local structure provide high complementarity to X-ray diffraction. Due to the need for radiation with tunable energy it is yet restricted to synchrotron sources. The Berlin Electron Synchrotron BESSY II operates multiple XAS stations for user service, some of which are particularly optimized for crystallographic problems:

mySpot [1] is optimized for mapping experiments with focus spot sizes as low as $1.5 \,\mu$ m. μ -EXAFS and μ -XANES in the energy range $5 - 25 \,$ keV can be combined simultaneously with small or wide angle scattering (SAXS & WAXS), X-ray fluorescence analysis (XRF), and Raman Scattering. Lateral focusing lenses with long focal length of 4-7 mm allows scanning of areas and volumes. The experiment is especially designed (but not limited to) for the study of hierarchically structured biological samples.

CryoEXAFS at KMC-3 beamline, developed in cooperation with Freie Universität Berlin [3], allows sample temperatures as low as 20 K, with convenient sample change at cold temperatures. Due to the absence of absorption in air, low radiation energies (3.6 - 14 keV) can be used, extending the range of observable light elements.

KMC-2 XANES [3] provides a stable beam in the energy range 4 – 15 keV, microfocus option and a selection of detectors, allowing transmission and fluorescence geometries. The open concept of the station allows the use of a wide range of sample environments, both in-house and user-provided, and flexible movement of the sample. A particular strong point is the suit of atmosphere control systems [4], which allows for continuous flow or volumetric control, high and low temperatures and pressures, precarious gases and, added most recently, humidity control.

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Keywords: EXAFS, XAS, Synchrotron

MS25-P04

Electron diffraction tomography of modulated minerals: the crystal structure of daliranite

Mauro Gemmi¹, Arianna Lanza¹, Enrico Mugnaioli¹, Luca Bindi², Werner H. Paar³

- Center for Nanotechnology Innovation@NEST, Istituto Italiano di Tecnologia, Pisa, Italy
- 2. Dipartimento di Scienze della Terra, Università di Firenze, Firenze, Italy
- 3. Department of Chemistry and Physics of Materials, University of Salzburg, Salzburg, Austria

email: mauro.gemmi@iit.it

Daliranite is a mineral originally discovered in 2003 at Zarshouran, northwest Iran, and approved by IMA in 2007 with the formula PbHgAs₂S₆. It occurs as matted nests of acicular crystals usually associated with quartz and orpiment. Single-crystal needles are just several hundreds of nanometers in size. On the basis of zone-axis electron diffraction patterns, daliranite was recognized as monoclinic, 19 Å x 4 Å x 23 Å and b =115°, with possible space groups P2, Pm or P2/m. The unit cell was confirmed by powder X-ray diffraction, however no structure solution was achieved and its crystal structure remained unknown [1].

The daliranite structure problem is a perfect candidate to be tackled using electron diffraction tomography (EDT). This method allows collecting 3D electron diffraction data on coherent domains having size of few hundreds of nanometers, like a single crystal X-ray diffractometer equipped with an area detector [2].

EDT data collected on isolated squared pieces of 200 nm of broken acicular crystals reveals that daliranite is exhibits a modulated structure with the main reflections that can be indexed with an orthorhombic cell having a = 9.5 Å b = 4.3Å c = 21 Å and extinction symbol Pc n. The modulation is along a ($\mathbf{q} = \alpha \ 0 \ 0$) with α varying from crystal to crystal in the range between 0.33 and 0.25. The average structure of daliranite can be solved in space group *Pcmn*. The resulting structure shows a chemical formula that differs from that originally reported: PbHgAs₂S₅, which does not require the presence of $(S_2)^2$ in the structure. The average structure is formed by zig-zag chains of PbS₈ bicapped trigonal prisms running along a, laterally connected by linear HgS2 and As₂S₆ dimers. In order to discover the mechanism behind the modulation we integrated the superstructure reflections from a crystal with $\mathbf{q} = 0.25 \ 0 \ 0$ and analyzed them with a superpace approach using JANA2006. The modulated structural model obtained in the 4D space group Pcmn $(\alpha 00)0s0$ can be refined and indicates that the modulation is due to shifts of the As atoms of the dimers along b, forming alternatively dimers parallel or inclined with respect to the ac plane. It is highly remarkable that EDT can furnish data reliable for structure investigation of modulated structures on such small crystal grains, where in fact zone-axis electron diffraction and powder X-ray diffraction even failed in the unit cell determination.

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Keywords: Electron diffraction, modulated structure, daliranite

MS25-P05

Application of laboratory X-ray diffraction equipment for Pair Distribution Function (PDF) analysis

Milen Gateshki¹, Marco Sommariva¹, Detlef Beckers¹, Stjepan Prugovecki¹, Martijn Fransen¹

1. Malvern Panalytical B.V., Almelo, Netherlands (Holland, Europe)

email: milen.gateshki@panalytical.com

The increased interest in recent years regarding the properties and applications of nanomaterials has also created the need to characterize the structures of these materials. One of the most promising techniques to study nanostructures using X-ray diffraction is by using the total scattering (Bragg peaks and diffuse scattering) from the samples and the pair distribution function (PDF) analysis. The pair distribution function provides the probability of finding atoms separated by a certain distance. From experimental point of view a typical PDF analysis requires the use of intense high-energy X-ray radiation (E \geq 15 KeV) and a wide 2 θ range. At present, synchrotron and neutron sources are the preferred choice for PDF analysis, but there is clearly an increasing need for a PDF solution based on laboratory diffraction equipment. Such a solution, though limited, will benefit areas where quick feedback about the materials properties is important and will allow the routine application of PDF analysis for materials characterization in university laboratories as well as industrial R&D departments.

After the initial feasibility studies regarding the use of standard laboratory diffraction equipment for PDF analysis [1,2] this application has been further developed to achieve improved data quality and to extend the range of materials, environmental conditions and geometrical configurations that can be used for PDF experiments. The recent introduction of detectors with improved efficiency for high-energy X-rays [3] has further enhanced the capabilities of laboratory diffractometers for total scattering experiments. This contribution presents several examples of laboratory PDF studies performed on different nanocrystalline and amorphous materials of scientific and technological interest (organic substances, oxides, metallic alloys, materials for battery applications, etc.) and demonstrates that PDF analysis with a laboratory diffractometer can be a valuable tool for structural characterization of nanomaterials



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Keywords: Pair Distribution Function, Total scattering, Nanomaterials

MS25-P06

Ab initio structure determination from unindexed powder patterns by a global optimization approach using pattern comparison based on cross-correlation functions

Stefan Habermehl¹, Carina Schlesinger¹, Martin U. Schmid¹

1. Institute of Inorganic and Analytical Chemistry, Goethe-University Frankfurt/Main, Frankfurt/Main, Germany

email: habermehl@chemie.uni-frankfurt.de

A method for *ab initio* structure determinations from powder diffraction data (SDPD) of organic compounds, which does not require prior indexing of the experimental pattern, has been developed. The global optimization approach is based on the direct fit of random trial structures to the powder data using an algorithm called FIDEL ("FIt with DEviating Lattice parameters"). It uses a similarity measure based on cross-correlation functions, which allows the comparison of simulated and experimental powder data even if the lattice parameters do not match [1,2].

The structure determination process starts with the molecular geometry of the compound and a global search space setup in various crystal symmetries. The lattice parameters, molecular position and orientation, and selected intramolecular degrees of freedom are fitted simultaneously in an elaborated multi-step procedure. The hierarchical search strategy developed is based on similarity screening, structure fitting and iterative adaptation of parameter ranges. It combines various methodologies in order to realize an efficient and effective exploration of the global search space. The standard procedure includes an adaptive mechanism for the balancing of computing time spent on the generation of random structures, similarity screening, fitting and clustering of structural models. The structure determination proceeds stepwise from e.g. more than 20 million trial structures to a small number of promising structure candidates that are subjected to an automated Rietveld refinement with TOPAS [3]. Finally, a user-controlled Rietveld refinement with TOPAS is performed.

By exploiting the full potential and versatility of the pattern comparison approach based on cross-correlation functions and supported by the integration of 3rd party components, a complete SDPD framework evolved, that covers almost all scenarios of finding crystal structures corresponding to given experimental data.

The global optimization approach presented is suitable for a wide range of "problematic" powder patterns, including powders of low crystallinity, non-phase-pure samples or disordered structures. While pushing SDPD to its limits, applications of the method deliver valuable insights into ambiguities arising from low-quality experimental data, where the "one powder – one structure" paradigm of SDPD is beginning to collapse. Even if the results do not converge into a single solution qualifying as a publication grade structure determination, the method can provide a set of structural models that match the powder as much as possible, for further analysis.

Examples of (metal-)organic compounds are shown, including the previously unknown structures of nanocrystalline phases of 2,9-dichloro- and 4,11-difluoro-quinacridone solved from powder patterns with 14-20 peaks only.

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Keywords: structure determination from powder data, global optimization, cross-correlation functions



Associating X-ray structure and antioxidant activity through UV-vis spectroscopy, cyclic voltammetry and DFT methods in Emodin

Miriam Rossi¹, Stuart Belli¹, Kelly Wen¹, Francesco Caruso¹

1. Department of Chemistry, Vassar College, Poughkeepsie, NY, United States of America

email: rossi@vassar.edu

Regulation of reactive oxygen species such as the superoxide ion is an important chemical process. Emodin (1,3,8-trihydroxy-6-methyl anthraquinone) is present in the root and rhizome of *Rheum palmatum*, and the goji berry (*Lycium barbarum* and *Lycium chinense*). Elucidating the manner in which emodin carries this out may provide insight into the chemical properties described in the literature.

The scavenging of the superoxide radical in this study was analyzed using a combination of several methods. We quantify the ability of emodin in scavenging the superoxide ion O_2 — in an aprotic solvent, dimethyl sulfoxide (DMSO); since water interferes with superoxide, highly dehydrated DMSO was used. We describe the results of our antioxidant assay using the electrochemical method of cyclic voltammetry with a novel rotating ring disk electrode (RRDE) method. This powerful technique provides a quantitative measurement of a redox reaction and allows us to detect products, side-products or even short-lived intermediates of electrode reactions. Since this process was accompanied by a variation of color, the time evolution of this antioxidant process was followed using in situ UV-Vis spectroelectrochemistry. At the molecular level, the reactivity of this process was followed using DFT methods which could be applied after determination of the crystal structure using single crystal X-ray diffraction. The combination of these different methods allowed us to demonstrate the unusual manner in which emodin behaves when scavenging superoxide radical. Our results point to the importance of the electron transfer in this scavenging mechanism.

Keywords: antioxidant activity, cyclic voltammetry, emodin

MS26- Aperiodic and modulated structures

Chairs: Prof. Sven Lidin, Prof. Alla Arakcheeva

MS26-P01

Polarisation via local ordering mechanisms

Emma Wolpert¹, Alistair Overy¹, Peter Thygesen¹, Arkadiy Simonov¹, Mark Senn², Andrew Goodwin¹

- 1. Department of Chemistry, University of Oxford, Oxford, United Kingdom
- Department of Chemistry, University of Warwick, Coventry, United Kingdom

email: emma.wolpert@chem.ox.ac.uk

Systems containing correlated disorder are becoming more and more prevalent in materials science.1 Thus understanding and exploring the disorder-property relationship is becoming of greater importance. In our work2 we focussed on how aperiodic systems could lead to a macroscopic polarisation. Using classical Monte Carlo simulations, we study a simple statistical mechanical model from local displacements on the square and cubic lattices. Our model contains two key ingredients: a Kitaev-like orientation-dependent interaction between nearest neighbours, and a steric term that acts between next-nearest neighbours. Taken by themselves, each of these two ingredients drives its own form of local ordering to a non-polar disordered phase with a manifold of degenerate ground states. These phases are incapable of driving long-range symmetry breaking, despite the presence of a broad feature in the corresponding heat capacity functions. Instead each ingredient results in a "hidden" transition on cooling to two distinct types of local order. Remarkably, their intersection i.e. the ground state when both interaction contributions are invoked leads to a disordered, but polar, phase which has conceptual parallels to tetragonal BaTiO₃ or KNbO3.3 These key ingredients could potentially be utilised in future material design

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Keywords: polarisation, correlated disorder

MS26-P02

Polymorphism of NiSeO₃(H₂O) studied on multiphase crystals

Morgane Poupon¹, Nicolas Barrier², Olivier Perez², Michal Dušek¹, Václav Petříček¹

- 1. Department of Structure Analysis Fyzikální Ústav AV ČR, v. v. i, Prague, Czech Republic
- 2. CRISMAT Laboratory, CAEN, France

email: poupon@fzu.cz

Inorganic materials with a layered structure are interesting for their potential exchange and/or storage properties [1]. These structures typically have weak intermolecular bonds between their different layers, like Van der Waals or hydrogen bonds [2]. However, weak bonds may lead to stacking faults or the intergrowth of phases inside the crystal. These defects could induce diffuse scattering and additional reflections, which can be observed on the reciprocal planes reconstructed from X-ray single crystal measurement. Understanding this complex order can allow us to solve structures of metastable polymorphs and to apprehend the processes of transformation towards their stable states. The family of lamellar compounds MSeO3(H2O) (M = Mn, Co, Ni, Zn, Cd) [3] is of interest regarding their several polymorphs. The cohesion of these structures is provided by hydrogen bonds. The NiSeO3(H2O) crystals were synthesized using hydrothermal synthesis under lowpressure and low temperature conditions.

We will present how the formalism of (3 + 1)d superspace can help to reveal the crucial role of weak interaction and the existence of intergrowth between two polymorphs in the crystal. Then, we will present the temperature stability study using low and high-temperature single crystal X-ray diffraction measurements of these multiphase crystals. References:

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Keywords: Hydrogen, Layers, Superspace

MS26-P03

FeSbO₄ and other rutile type mixed-oxides revealing nano-structural flexibility

Jon Canca¹, Jorge Hernández-Velasco¹, Ángel Landa-Cánovas¹, Fernando Agulló-Rueda¹

 Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC), Madrid, Spain

email: jon.canca@csic.es

There are many examples of rutile-type mixed oxides that are active and selective catalysts for the ammoxidation of propane into acrylonitrile [1] (VSbO₄, FeSbO₄, FeVSbO₆, CrSbO₄ ...). In this way, many studies have focused on the structural flexibility shown by rutiles when different cations and oxidation states are added.

 $Fe_{0.5\star}V_{2s}Sb_{0.5\star}O_2 \ (0 \le x \le 0.4)$ solid solutions were prepared by solid-state reaction from their raw oxides (Fe_2O_3, Sb_2O_3) and $V_2O_3)$, using an air or argon atmosphere depending on the composition. The obtained samples were characterized by powder x-ray diffraction, electron diffraction, XEDS analysis, EELS spectroscopy, micro-Raman spectroscopy and magnetic susceptibility measurements.

Even though FeSbO₄ has been deeply studied [2], some doubts remain about the iron oxidation state and cation ordering. In this sense, electron diffraction patterns reveal a reciprocal lattice where diffuse reflections suggest a 3-fold trirutile along *c*-axis. The weak intensity of these reflections may indicate that only small clusters of the crystal are ordered into a trirutile type superstructure, the rest of the crystal is still crystallizing as a simple rutile. It is argued that only the presence of Fe²⁺ can produce this superstructure. Thus, EELS spectroscopy analysis and magnetic susceptibility measurements were made in order to find out if Fe²⁺ is present. The obtained results do not exclude this hypothesis.

With the purpose of keeping on studying the structural modification of rutile type oxides, vanadium was partially substituted in FeSbO₄ preparing the next composition series: Fe_{0.5-x}V_{2.x}Sb_{0.5-x}O₂. Due to the difficulty of three cations have to be ordered in the same atomic position [3], no superstructure reflections are observed by electron diffraction. However, in the compounds with high iron contents, weak diffuse intensity indicative of short-range order (SRO) phenomena is found by electron diffraction.

In conclusion, these compounds, which are studied due to their catalytic properties, show very interesting order-disorder phenomena because of the extraordinary structural flexibility of these phases. The different characterization of each compound and its particular structural order will be reported.



Selected area electron diffraction patterns for FeSBO4 (a) and FessVscSbcsO((b). Magnetic susceptibility as function of T (c) and (d)

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Keywords: Rutile,flexibility

MS26-P04

Exploring modulation in molecular crystals at low temperatures

Marcin Sztylko1, Anna Hoser1

1. Faculty of Chemistry, University of Warsaw, Warsaw, Poland

email: marcin.sztylko@gmail.com

Technical progress in crystallographic instruments allows contemporary crystallographers to more routinely conduct low-temperature diffraction measurements. Additionally, modern diffractometers have stronger sources and more sensitive detectors than they had a few years ago. As a consequence, even crystal structures that have been extensively studied at ambient conditions start to reveal their more complex nature. The importance of low-temperature measurements is discussed for polymorphs of 4'-hydroxyacetophenone (HAP)¹.

For this enantiotropic polymorphic system, we collected single crystal X-ray diffraction data in the temperature range from 30 K to 330 K. At 123 K orthorhombic form II of HAP appears to be a new, commensurately modulated structure with a modulation vector q = [0.4, 0.0, 0.0]. The structure can be solved in a supercell with 10 molecules in the asymmetric unit. Interestingly, further lowering of temperature down to 30K resulted in a discovery of a new, incommensurately modulated phase with 4 independent molecules and crystal lattice of the P21 space group and modulation vector q = [0.37, 0.17, 0.0]. Consequences of modulation for the relative stability of polymorphs will be discussed.



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Keywords: polymorphism, commensurate modulation, incommensurate structure

MS26-P05

Unraveling the structure of Vaterite using precession electron diffraction tomography

Gwladys Steciuk1, Daniel Chateigner2, Lukáš Palatinus

- 1. Department of Structure Analysis , Institute of Physics CAS (FZU) Na Slovance 2, 182 21, Prague, Czech Republic
- 2. CRISMAT-ENSICAEN Laboratory (CNRS UMR6508), IUT Caen, Caen Normandie University., Caen, France

email: gwladys.steciuk@gmail.com

Among the three crystallized anhydrous polymorphs of CaCO₃, vaterite is the least stable form under natural conditions and has been identified as a constituent of various biominerals such sea crustaceans, mollusk pearls, fish otoliths ascidians and even human organic tissues (heart valve) or plants. As a metastable phase, vaterite is involved in the first step of crystallization of the two stable calcite and aragonite polymorphs and in several carbonate-forming systems. Its complete structural determination would consequently shed important light to understand scaling formation and biomineralization processes. While vaterite hexagonal substructure $(a \approx 4.1 \text{ Å and } c \approx 8.5 \text{ Å})$ and the organization of the $(CO_3)^{2-1}$ and Ca2+ within a single layer is known, conflicting interpretations regarding the stacking sequence remain and preclude the complete understanding of the structure. Indeed, earlier workers reported the presence of additional Bragg peaks and diffuse features in diffraction patterns of vaterite together with twinned domains, and the likely coexistence of several polymorphs [1-2].

In order to resolve the ambiguities in the structural description of vaterite, we performed precession assisted electron diffraction tomography (PEDT) to collect single crystal data on beam sensitive nanocrystalline vaterite. Several data sets were collected with low-dose technique at low-temperature with a nano-size beam and processed using programs PETS, Jana2006 and Dyngo [3]. Our results unambiguously demonstrate that vaterite grows up mostly as a coherent intergrowth of two ordered and twinned polymorphs having the same composition. Their structures were solved ab initio and described as commensurate modulated structures. The models were refined against electron diffraction data using the dynamical refinement procedure including both modulation and twins. Our results are also consistent with Rietveld refinement from x-ray powder data [3] at low and ambient temperature. This study brings a new perspective by giving a better understanding of the existing stacking sequences and the possible rotations of the $(CO_3)^2$ groups in vaterite.

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Keywords: vaterite, precession electron diffraction tomography, intergrowth

MS27- Quasicrystals: theory and experiment

Chairs: Prof. Marc de Boissieu, Prof. Janusz Wolny

MS27-P01

AlCuRh decagonal quasicrystal – new techniques for the refinement

Ireneusz Buganski1, Radoslaw Strzalka1, Janusz Wolny1

1. AGH University of Science and Technology, Faculty of Physics and Applied Computer Scinece, Krakow, Poland

email: irek910329@gmail.com

Quasicrystals are still challenging when it comes to the structure refinement. The complexity of the structure requires the use of sophisticated mathematical models to properly describe the structure. In addition, the range of diffraction peaks' intensities is wide with small peaks especially being affected by multiple disorder effects which are still not included in the refinement. What is important those small peaks carry essential structural information and without them the structure model cannot be considered correct. Recently we invented and applied a variety of new models [1, 2] to describe the structure of decagonal AlCuRh quasicrystal. The quality data allows us to test which approach could be beneficial for the refinement. We testes new phononic correction assuming local statistical deviation obeying sinusoidal oscillations resulting in the Bessel function in the Foureir space. We also included phason flips in the quasilattice of the Penrose Tiling, providing long-range order, to correct for the deviation of the structure units locations. Last but not least, we phenomenologically included the effect of the multiple scattering which appears to be a significant effect in terms of weak reflections. All those corrections have proven to improve the quality of agreement between theoretical model and the experimental data. In the best fit we could obtain an R-factor equal to 5.84%, which is the best result yet for the quasicrystal. In the presentation we explain the reasons for the application of each corrective term and the effect on the final structure model.

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Keywords: quasicrystals, phason disorder, structure refinement

MS27-P02

Statistical method of structural description of complex systems

Janusz Wolny¹, Ireneusz Bugański¹, Radosław Strzałka¹, Joanna Śmietańska¹

1. Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Krakow, Poland

email: wolny@fis.agh.edu.pl

The statistical method is a commonly approved and confirmed by many results approach to structural and diffractional studies of crystals. It is particularly successful in terms of complex systems, like modulated crystals or quasicrystals. In our presentation we will show the fundamentals of the method, including the basic concept behind – called the average unit cell concept [1], and discuss its application to modulated crystals and quasicrystals [2,3].

The average unit cell is the probability distribution function P(u) of atomic positions calculated against some periodic reference lattices. A Fourier transform of P(u) gives the diffraction pattern. Structural modeling within the statistical approach involves a modeling of the P(u) distribution, which is an object in physical space, and enables including all kinds of structural disorder in a derivation of the structure factor. We will show how this methodology applies for the harmonically modulated crystal (with harmonic modulation and incommensurate scattering vector), including its correspondence to a quasicrystal, and selected decagonal quasicrystals.

The method has no limit in applying it also to such complex systems, like proteins of macromolecules, where the structural disorder appears to play a crucial role, and attempts to use crystallographic methods known for periodic crystals are rather doubtful. We will shortly introduce a possible benefits from applying the statistical method to complex organic systems.

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Keywords: structure modeling, statistical method, complex systems

MS28- Magnetic order: methods and properties

Chairs: Dr. Francoise Damay, Prof. José L. García-Muñoz

MS28-P01

Phase transition of a spiral magnetic ordering in the Fe-based double-perovskite

Chao-Hung Du¹, Chun-Hua Lai¹, Yu-Hui Liang¹, Yen-Chung Lai², Chin-Wei Wang², Kirrily C. Rule³, F.-C. Chou⁴, S. Yano²

- Department of Physics/Tamkang University, Tamsui 25137, New Taipei City, Taiwan
- National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan
- 3. Australian Center for Neutron Scattering, NSW 2232, Australia
- Center for Condensed Matter Science/National Taiwan University, Taipei 10617, Taiwan

email: chd@mail.tku.edu.tw

Using a modified traveling solvent floating zone technique, we are able to grow a high quality single crystal of the double perovskite oxide YBaCuFeO5 for the detailed study using magnetization, dielectric constant, and neutron diffraction. We demonstrate that the crystal shows two antiferromagnetic transitions at $T_{NI} \sim 475$ K and $T_{N2} \sim 175$ K, and displays a giant dielectric constant with a characteristic of the dielectric relaxation at T_{N2} . It does not show the evidence of the electric polarization for the crystal. The transition at T_{NI} corresponds with a paramagnetic to antiferromagnetic transition with a magnetic propagation vector doubling the unit cell along three crystallographic axes. Such a paramagnetic state at high temperatures was also confirmed by the using inelastic neutron scattering. Upon cooling, at T_{N2} , the commensurate spin ordering transforms to a spiral magnetic structure with a propagation vector of $(0.5h \ 0.5k \ 0.5l+-\delta)$, where h, k, and l are odd, and the incommensurability is temperature dependent. Around the transition boundary at T_{N2} , both commensurate and incommensurate spin ordering coexist.

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Keywords: phase transition, spiral magnetic ordering, neutron scattering

MS28-P02

Neutron powder diffraction study of $Tm_2Mn_2O_7$ and $Y_2Mn_2O_7$ - pyrochlore obtained by yet another chemical route of synthesis

Ekaterina Pomjakushina¹, Katharina Rolfs², Janusz Karpinski², Kazimierz Conder¹, Vladimir Pomjakushin³

- 1. Laboratory for Multiscale Materials Experiments, Paul Scherrer Institut, Villigen, Switzerland
- Laboratory for Development and Methods, Paul Scherrer Institut, Villigen, Switzerland
- Laboratory for Neutron Scattering and Imaging, Paul Scherrer Institut, Villigen, Switzerland

email: ekaterina.pomjakushina@psi.ch

The rare earth manganese (IV) pyrochlores cannot be synthesized at ambient pressure requiring high pressures for the stabilization of the pyrochlore lattice, which is mainly due to the small size of Mn (IV) compared to trivalent rare earth cations. All of these materials appear to be ferromagnets. Neutron studies of some selected A2Mn2O7(Y, Ho, Yb) were done, but still more work is needed to completely characterize their magnetic ground state. We present yet another chemical way of synthesis of Tm₂Mn₂O₇ [1] and Y₂Mn₂O₇ [2] pyrochlores and the studies of their magnetic and crystal structures by high resolution neutron powder diffraction. Both compounds are single phase pyrochlores $(Fd3^{-}m)$ at room temperature. On cooling below about 30K they show the transitions to the ferromagnetic state with additional antiferromagnetic (AF) canting on only one sort of atoms for Tm₂Mn₂O₇. The magnetic structure has magnetic Shubnikov group $I4_1/am'd'$ with the tetragonal distortion and large magnetostrsiction (especially for A=Y) refined from the diffraction data. The presence of AF canting in both compounds with magnetic (Tm) and nonmagnetic (Y) A-cation allows us to assign AF-ordering to Mn-sublattice.

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 V. Pomjakushin et al, to be published

Keywords: magnetic structure, pyrochlore

MS28-P03

On Magnetic and Crystal Structures of NiO, MnO

Pomjakushin Vladimir¹

 Lab. for Neutron Scattering, Paul Scherrer Institute, Villigen, Switzerland

email: vladimir.pomjakushin@psi.ch

Since the first neutron diffraction studies of manganese and nickel monoxides [1] the interest to the magnetic and crystal structures of MnO and NiO is kept up, see e.g. experimental study [2] and theoretical first principal calculations [3] and references cited therein. It is well established experimentally that below N eel temperature the crystal structure is metrically lowered in symmetry from cubic Fm3m to rhombohedral R3m, or might be to monoclinic one. However, the allowed by symmetry monoclinic distortions from rhombohedral R3m-metric are very small and the explicit monoclinic splittings of the diffraction peaks have not been experimentally observed. We analyse in full details all possible magnetic crystallographic models metrically compatible with the experiment by using isotropy subgroup representation approach based on the propagation vector star. The models (some not previously considered) are compared with the high resolution and high intensity diffraction data measured at the HRPT diffractometer at Swiss neutron spallation source SINQ.

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Keywords: magnetic, structure, symmetry,

MS28-P04

Crystal chemistry features and physical properties of three Mn phosphates

Larisa Shvanskaya¹, Olga Yakubovich¹, Galina Kiriukhina¹, Alexander Vasiliev¹

1. M.V. Lomonosov Moscow State University, Moscow, Russia

email: lshvanskaya@mail.ru

The complex phosphates with manganese cations in low oxidation state (Mn^{2^+}) attract attention as potential catalysts for industrially important oxygen reduction reactions [1]. For example, $Mn_3(PO_4)_2^*$ 3H₂O are found to display interesting electrocatalytic properties for water splitting [2]. Besides catalytic activity, Mn-based phosphates can demonstrate rare magnetic grounds states, which make these compounds attractive both for experimental physical property investigation and for theoretical calculation.

Three manganese phosphates, namely RbMn₄(PO₄)₃(I), CsMnPO₄(II) and Mn₂PO₄OH(III) were studied by single crystal X-ray diffraction and characterized by measuring of the magnetic susceptibility, magnetization, and heat capacity. The RbMn₄(PO₄)₃ belongs to the morphotropic series of oxo-salts with general formula AM4(TO4)3. The Mn2PO4OH presents a manganese end-member of the triplite-triploidite family. The (I,III) crystal structures can be described as three-dimensional frameworks of corner and edge-sharing MnO5 and MnO6 polyhedra which are further straightened by PO4 tetrahedra. CsMnPO4 presents a novel polymorphic modification with zeolite ABW-type framework consisting of tridimite-like sheets of six-membered rings of manganese and phosphorus tetrahedra sharing vertices. The magnetic ground states of (I) and (II) are canted antiferromagnet below $T_N = 3.1$ K and $T_N = 4.7$ K, respectively. The Mn_2PO_4OH compound orders antiferromagnetically at $T_N = 4.6$ K. In general, the magnetic behavior of CsMnPO4 is similar to that of structurally related RbMnPO₄ [3]. Despite three dimensional magnetic structures of RbMn₄(PO₄)₃ and Mn-₂PO₄OH, both phosphates demonstrate low dimensional magnetic behavior. Their specific feature is the high ratio of Weiss and Neel temperatures $|\Theta| / T_N$, called frustration parameter. This value is equal to 10 for RbMn₄(PO₄)₃ and is twice as high for Mn₂PO₄OH. The origin of high frustration degree in the second compound is associated with the twisted saw tooth chain geometry of corner sharing triangles of manganese polyhedra (Fig.1, left), which may be isolated within tubular fragments of its crystal structure. The chain of another topology (Fig.1, right) is seemingly responsible for significant frustration in RbMn₄(PO₄)₃. The finite magnetization of $RbMn_4(PO_4)_3$ observed for $T < T_N$ might be explained by a Dzyaloshinskii-Moriya interaction.

Our investigation led us to establish the relation between the crystal structure and thermodynamic properties.

The work was supported by the Russian Foundation for Basic Research (grant No. 18-03-00908).

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Keywords: phosphates, crystal chemistry, antiferromagnet

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MS28-P05

Magnetic Raman scattering and symmetry analysis of complex-structure antiferromagnets Ni₂NbBO₆ and Fe₃BO₆

Mikhail Prosnikov¹, Sergei Barilo², Nadezhda Lyubochko², Sergei Shiryaev², Alexander Smirnov¹, Valery Davydov¹, Roman Pisarev¹

- 1. Ioffe Institute, Saint Petersburg, Russia
- 2. Institute of Solid State and Semiconductor Physics, Minsk, Belarus

email: yotungh@gmail.com

Isostructural orthorhombic crystals Ni₂NbBO₆ and Fe₃BO₆ belong to the *Pnma* (#62) space group [1] and manifest 3D long-range AFM transitions at T_N=23.5 K [2] and T_N=508 K, respectively. Such difference in transition temperatures is mostly due to different connectivity; while in Ni₂NbBO₆ magnetic ions occupy only the general 8*d* positions, in Fe₂BO₆ they are located in the 8*d* and 4*c* ones, which results in complitely distinct magnetic structures and superexchange paths. Other characteristic feature of Fe₃BO₆ is a presence of a weak ferromagnetic moment, which is spontaneously reoriented from [100] to [001] axis at T_{so}=415 K. Thereby, these systems offer an unique playground to explore static/dynamic magnetism and symmetry requrements for the existance and orientation of the weak ferromagnetic moment.

We present the experimental results on the crystal growth and studies of both lattice and magnetic dynamics, and their interaction in single crystals of Ni2NbBO6 and Fe3BO6 with the use of the polarized Raman spectroscopy in a wide temperature range 10-550 K. Nontrivial spin-phonon interaction with different signs of coupling constant depending on particular phonon mode was observed at T_N. In the AFM phases several magnetic modes of different nature were registered, including two-magnon ones. Methods of magnetic space groups and irreducible representations were used to determine the set of magnetic subgroups compatible with experimental observations. Appropriate Hamiltonians including several isotropic exchange and single-ion anisotropy constants were suggested for describing two-magnon excitations within the linear spin wave theory. Thus we were able to show that magnetic Raman scattering supported by symmetry analysis could be used for determinationof magnetic structures and exchange/anisotropy parameters [3].

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Keywords: magnetic Raman scattering, symmetry analysis, magnetic space group

MS29- Mathematical crystallography: special aspects of symmetry and other topics

Chairs: Prof. Berthold Stöger, Prof. Bernd Souvignier

MS29-P01

Towards objective crystallographic symmetry classifications of noisy 2D periodic images

Peter Moeck1, Andrew Dempsey1

1. Nano-Crystallography Group, Department of Physics, Portland State University, Portland, Oregon, United States of America

email: pmoeck@pdx.edu

Crystallographic symmetry classifications of noisy 2D periodic images are currently made on the basis of the three traditional plane symmetry deviation quantifiers of electron crystallography [1]. These quantifiers are, however, "pure distance measures" that are unable to deal with crystallographic supergroup-subgroup relationships and pseudo-symmetries in an objective manner [2]. A consequence of this is that the model with the lowest symmetry, i.e. the one which possesses the highest number of free parameters, fits noisy experimental data best. A version of Hamilton's well known R-factor ratio test [3] of mainstream 3D crystallography can be applied in principle, but is of limited utility because it is a null hypothesis test.

Objective crystallographic symmetry deviation quantifiers that properly account for crystallographic supergroup-subgroup relationships and pseudo-symmetries have recently been derived for noisy 2D periodic images on the basis of geometric Akaike Information Criteria (G-AICs) [2] and associated Akaike weights. (Akaike weights represent the probability that a certain crystallographic symmetry model within a disjoint or non-disjoint model set is the one that minimizes Kullback-Leibler information loss when it is used to represent full reality.) These quantifiers are demonstrated in this contribution on examples for the first time.

Openly accessible synthetic 2D periodic images (https:// nmevenkamp.github.io/UnitCellExtraction/) have been utilized for our objective crystallographic classifications with respect to their Bravais lattice types, Laue classes, and plane symmetry groups. The example images possess per design both genuine pseudo-symmetries and added Gaussian noise, which turned genuine symmetries into pseudo-symmetries of the second kind. Note that genuine symmetries constitute the symmetry group structure of the hypothetical noise-free version of an image, but are unavoidably disturbed by noise in any real world imaging process.

Genuine pseudo-symmetries and pseudo-symmetries of the second kind also cause problems in mainstream single crystal X-ray crystallography [2] so that the approach of this contribution should be generalized to the 3D case in order to achieve a larger impact. A few percent, i.e. tens of thousands, of the molecule and crystal structures in the major 3D crystallography databases have been mis-classified with respect to their crystallographic symmetry [2]. This is due to

the inherent subjectivity of the currently practiced approach where pure distance measures are utilized. When generalized to 3D, the above mentioned G-AIC approach [2] combined with Akaike weights will lead to superior noise-level dependent crystallographic symmetry classifications and subsequent re-assignments of mis-classified 3D structures to a range of symmetry types, classes, and groups where the probabilities of belonging to certain classifications is in each case quantified in an objective way.



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Keywords: Geometric Akaike Information criteria, crystallographic symmetry classifications, genuine pseudosymmetry

MS29-P02

Multidimensional crossed cube tilings

Shelomo Ben-Abraham1

1. Department of Physics, Ben-Gurion University of the Negev, Beer Sheba, Israel

email: shelomo.benabraham@gmail.com

The two-dimensional squiral (square spiral) tiling is an example of a non-pisot substitution tiling with singular continuous Fourier spectrum. Baake and Grimm invented the crossed square lattice substitution tiling as a simple equivalent to the squiral tiling [1]. I generalize this tiling to arbitrary dimension and call it "crossed cube tiling". I explicitly show its three- and four-dimensional instances. The method is valid in any dimension from zero to countable infinity but the size of the tiling grows exponentially and becomes quite impracticable in dimensions five and more.

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Keywords: squiral, crossed cube tiling

MS30- Halogen and chalcogen bonding in the solid state

Chairs: Dr. Guillermo Minguez, Prof. Giuseppe Resnati

MS30-P01

Cl ... Cl halogen bonds and *N*-oxide ... *N*-oxide interactions in crystal structure of pentachloropyridine *N*-oxide

Agnieszka Rybarczyk-Pirek¹, Kinga Wzgarda-Raj¹, Marcin Palusiak¹

1. Department of Physical Chemistry, Faculty of Chemistry, University of Lodz, Lodz, Poland

email: agnesr@uni.lodz.pl

In comparison with other halogens, fluorine and chlorine atoms are present in a large number of active compounds of chemical and biological importance. However, fluorine in contrast to chlorine, is described as merely able to form halogen bonding because of its small polarizability. Recently, a trichloromethyl group has attracted our attention because of potential sigma effects on chlorine halogen bonding. Our studies indicated that C-CL...O interactions may be classified as relatively strong ones, especially when enhanced by cooperative effect. The obtained results focus our attention on obtaining novel halogen bonding stabilized *crystal structures*. Our project involves utilizing various groups of potential halogen bonding acceptors in obtaining crystal structures with novel types of halogen bonds (XB), among them to *N*-oxide group as a potential XB acceptor.

The properties of the *N*-oxide group as an effective electron donor in hydrogen and halogen bonds have been the subject of many studies. Aromatic *N*-oxides have been also successfully used in synthesis of novel cocrystal structures stabilized by hydrogen bonds. Taking into consideration all these remarks we have chosen pentchloropyridine *N*-oxide as an object of our studies.

XRD studies revealed however, that in the crystal state molecules are linked by C-C1...Cl halogen bonds and *N*-oxide groups take part in very short intermolecular *N*-oxide...*N*-oxide interactions instead of expected C-C1...O ones. There can be indicated infinite planar ribbons od molecules linked by typical C1...Cl contacts and forming known from literature triangle aggregates - X₃ synthons in the crystal structure (see figure). These ribbons are furtherly ordered into herringbone motifs. A set of observed intermolecular interactions has been analyzed with the use of Hirshfeld surface tools.

Computations based on quantum chemistry methods (DFT- ω B97XD/6-311+G(d)) let us for a more detailed description of both kinds of intermolecular interactions. In the X₃ synthon non-additive effects are relatively low and rather meaningless in the chain of molecules linked by *N*-oxide...*N*-oxide interactions indicating in the both cases very small cooperative effects.



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Keywords: Halogen bonds, N-oxide group, energy of intermolecular interactions

MS30-P02

Cooperativity of halogen bonds – enhancing halogen bond donating ability of halogenated pyridines through halogen bonding with *N*-haloimides

Vladimir Stilinovic1, Dominik Cinčić

 University of Zagreb, Faculty of science, Department of chemistry, Zagreb, Croatia

email: vstilinovic@chem.pmf.hr

N-halogenated imides, common halogenating agents in organic synthesis, have recently been marked as extremely strong halogen donors. [1], [2], [3] In previous studies we have demonstrated that N-halogenated succinimides form extremely short XBs with halogen bond energies between 20 and 60 kJ mol-1, depending on the pyridine basicity and the halogen atom.[2] In light of rather high bond energies, it seemed possible for such halogen bonds to have a significant effect on the electron structure of both donor and the acceptor molecules, which in turn might be expected to affect the ability of the molecules to form additional intermolecular bonds in general and halogen bonds in particular. To test this supposition, we have prepared a series of cocrystals of N-haloimides (N-iodo- and N-bromosuccinimide, N-iodo- and N-bromosaccharin and N-bromophthalimide) with halogenated pyridine derivatives, thus introducing the possibility of a secondary halogen bond with halogenated pyridines as donors and imide oxygen atoms as potential acceptors.

In all the obtained crystal structures the expected halogen bond between the N-haloimide halogen and pyridine nitrogen was found to be present. However, the occurrence of a secondary halogen bond (as well as its geometry when it is present) was found to depend on both the halogen atom of the pyridine, but also the halogen bond donor ability of the N-haloimide. While secondary I-O contacts were present in all cocrystals of iodopyridines, the equivalent Br...O contacts with bromopyridines were generally found only in cocrystals with N-iodoimides (stronger halogen donors), due to a larger polarization of the bromopyridine by a stronger primary halogen bond. This difference in polarisation has been verified through the molecular electrostatic potential calculations which have shown that the maximal positive potential in the σ -hole of the bromine of a 3-bromopyridine involved in a strong halogen bond (with N-iodosuccinimide as halogen donor) is markedly higher than that in the free 3-bromopyridine or in 3-bromopyridine involved in a weaker halogen bond (with N-bromosuccinimide), and approaches the value for bromine in protonated 3-bromopyridinium cation. This strongly reflects on the structures of the cocrystals with no secondary Br ... O contacts in the structure of 3-bromopyridine-N-bromosuccinimide cocrystal, Br-O halogen bonds of ca. 3.11 Å in 3-bromopyridine-N-iodosuccinimide cocrystal and ca. 3.01 Å in ionic 3-bromopyridinium saccharinate which is isostructural with the N-iodosuccinimide cocrystal. The obtained results demonstrate that when several (inequivalent) halogen bonds are to be employed in engineering a crystal, their cooperativity (more generally, interdependency) must be taken into account.

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Keywords: halogen bond, cooperativity, N-haloimide

MS30-P03

The halogen C-Br...S bonding in the crystal structure of an oxazole derivative: a charge density study

Maciej Kubicki¹, Agata Owczarzak¹, Anita M. Grzeskiewicz¹, Tomasz Stefanski¹, Zbigniew Dutkiewicz²

- 1. Department of Chemistry, Adam Mickiewicz University in Poznan, Poznan, Poland
- 2. Department of Chemical Technology of Drugs, Poznan University of Medical Sciences, Poznan, Poland

email: mkubicki@amu.edu.pl

Microtubules are key components of the cytoskeleton consisting of $\alpha\beta$ -tubulin heterodimers and are involved in a wide range of various cellular functions, such as cell division, where they are responsible for mitotic spindle formation and proper chromosomal separation. The biological importance of microtubules in mitosis and cell division makes them an interesting target for the development of anticancer agents: many of them are already in clinical use (epothilone, paclitaxel) or in clinical trials such as combretastatin A-4 (3'-hydroxy-3,4,4',5-tetramethoxy-cis-stilbene, CA-4), however the search of new potent agents is still continued.

Our successful investigation on novel potent inhibitors of tubulin polymerization from group of CA-4 thioderivatives [1] prompted us to prepare a new series of oxazole-bridged CA-4 analogues. They were synthesized using the Van Leusen multicomponent reaction between corresponding benzaldehydes and *p*-toluenesulfonylmethyl isocyanides (TosMICs).

In the crystal structure of one of the new derivatives, namely 4-[3-bromo-5-methoxy-4-(methylsulfanyl)phenyl[-5-(4bromo-3-nitrophenyl)-1,3-oxazole, a very short and directional C-Br···S halogen bonding was found (Br···S 3.264Å, C-Br···S 168.8°). In fact, it is the shortest such distance in all organic structures found in the CSD. As we were able to prepare the crystals of very good quality, high resolution diffraction data were collected, up to $sin0/\lambda=1.10Å^{-1}$, and the electron density was modelled using Hansen-Coppens pseudoatom multipolar model [3]. The deformation density maps, together with the Atom-In-Molecules topological analysis of interactions will be presented in the communication. Also the comparison with the quantum chemistry calculations results show the importance of halogen bonding for the crystal structure.

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Keywords: halogen bonding, charge density analysis, critical points

MS31- The role of supramolecular interactions in polymorphs and co-crystals

Chairs: Dr. Laszlo Fabian, Prof. Mino R. Caira

MS31-P01

Polymorphism in a 2D Copper(I) coordination polymer based on a flexible ligand

Olaya Gómez-Paz¹, Rosa Carballo¹, Ezequiel M. Vázquez-López¹, Ana B. Lago²

- Departamento de Química Inorgánica, Instituto de Investigación Sanitaria Galicia Sur (IISGS) - Universidade de Vigo, E-36310 Vigo, Galicia, Spain
- Laboratorio de Rayos X y Materiales Moleculares, Departamento de Física Fundamental - Universidad de La Laguna., E-38204 La Laguna, Tenerife, Spain

email: olgomez@uvigo.es

Coordination polymers (CPs) based on organic flexible ligands are promising materials due to their potential dynamic behaviour. In addition, the use of such kind of ligands allows the formation of polymorphic isomers which can be isolated in certain synthetic and crystallization conditions.

In this work, we describe two polymorphic forms (1 $P2_{*}/c$ and 2 C2/c) for the 2D coordination polymer 2_{*} [CuCl(4bpytm)] containing the spacer bis(4-pyridylthio)methane (4bpytm) which has proven its conformational flexibility in other coordination polymers [1]. Both Cu(1) compounds are obtained by a hydrothermal procedure from Cu(11) precursors. Crystals of 1 are isolated from a reaction using busulfan or procainamide hydrochloride and crystals of 2 results from a direct reaction between the ligand and the Cu(II) salt. It is interesting to note that the type of arrangement observed here have been only scarcely observed for this ligand [2,3].

The two compounds are 2D networks achieved by the bridging role of 4bpytm ligand and the Cu_2Cl_2 core. The ligand in the two compounds shows very different torsion angles and this fact lets that (2) have got interpenetration in its laminar structure whereas in (1) the sheets are parallel stacked.



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Keywords: copper(I) complexes, coordination polymers, crystal structures, metallosupramolecular chemistry.

Sponge like structures assisted by hydrogen bonds

Tamas Holczbauer¹⁻², Laura Bereczki¹, Nóra Veronika May¹, Dániel Vajk Horváth², Roberta Palkó², Tibor Soós², Petra Bombicz¹

- Chemical Crystallography Research Laboratory, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Budapest, Hungary
- 2. Institute of Organic Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Budapest, Hungary

email: holczbauer.tamas@ttk.mta.hu

The appearance of the metal organic frameworks (MOFs) has opened a new branch of research, the new structures are suitable for as sensing, drug delivery, heterogeneous catalysis, separation and storage etc. Following the discovery of MOFs, new covalent organic frameworks (COFs) were synthesised as metal-free analogous. Recently highly porous hydrogen-bond assisted organic frameworks (HOF) were reported. Most of the published organic frameworks are electronically neutral, but some of them are ionic metal-organic frameworks (iMOFs) or ionic covalent organic frameworks (iCOFs). Intermolecular forces and molecular inflexibility are the conditions of the formation of non-covalently bonded organic frameworks.

Three different polymorphic- and solvatomorphic iHOF frameworks of the investigated molecule (1: 5,5,11,11-tetrabutyl-1,3,7,9-tetraphenyl-4,5,6,10,11,12-hexahydro-5,11- diazadibenzo[ef,kl]heptalene-5,11-diium-bromide) were prepared by using different crystallisation techniques and were structurally characterised using single crystal X-ray diffraction technique [1]. Crystals of 1a were obtained by recrystallization from the saturated THF solution in the presence of the solid powder of compound 1 in a closed ampule. 1a crystallizes in space group Fddd and almost the half of the unit cell (42%) was found to be filled with disordered THF solvent molecules. Br ions are placed along the channels close to the quaterner nitrogen groups. Crystals of 1b were grown by slow evaporation of the THF solvent, the dimorphic structure has the Pnna space group. In this case the void volume is ~39% per unit cell. The voids are filled with disordered solvent molecule similarly to 1a. The crystals of 1c were received by fast evaporation of the solvent mixture of THF and pyridine to almost dryness. The molecules crystallise in the $P2_1/n$ space group and contain voids of ~18% where the pyridine molecules take part in the framework construction as neutral linkers. 1a and 1b are polymorphs of 1, while 1b and 1c are solvatomorphs.

In all reported three crystalline frameworks the structures are stabilized by C-H...Br and Br... π interactions, while pyridine is part of C-H... π interactions. The solvent THF molecules are disordered throughout the channels. The residual electron density in the channels could be taken into account by the refinement of the data with squeeze program (part of the Platon program). The necessity of molecular inflexibility in the formation of these highly porous crystals is also discussed.

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Keywords: Hydrogen-bonded Organic Framework, Porous materials, polymorphs, solvatomorphs

MS31-P04

Synthesis, structure and chemical properties of copper(II) complexes with 2,2'-bipyridine and L-serine: porous materials and polymorphism

Darko Vušak¹, Biserka Prugovečki¹, Dubravka Matković-Čalogović¹

1. Department of Chemistry, Faculty of Science, University of Zagreb, Zagreb, Croatia

email: dvusak@chem.pmf.hr

Considering copper as an essential metal and being the key element for regular function of some proteins, copper(II) complexes with amino acids are often used as model systems for metal-protein interactions.[1] Furthermore, copper(II) complexes with heterocyclic bases and amino acids readily interact with DNA molecules through hydrogen bonds and π -interactions. These comopunds showed prominent antiproliferative activity against a series of tumor cell lines.[2] Since 2,2'-bipyridine and serine are capable of forming various types of noncovalent interactions, their complexes may form predictible supramolecular motifs, thus being important in crystal engineering. In our latest research we have prepared porous complexes of copper(II) with 1,10-phenantholine and L-serine which we were able to interconvert into each other in the solid state under controlled conditions.[3]

Herein, we present the first four crystal structures of copper(II) complexes with 2,2'-bipyridine (bpy) and L-serine (ser) obtained by fine tuning of synthetic conditions: $[Cu(ser)(H_2O)(bpy)]_2SO_4$ ($3H_2O$ (1), $[Cu(ser)(bpy)]_2SO_4$ ($3H_2O$ (1), $[Cu(ser)(bpy)]_2SO_4$ (3a and 3b). The two complexes with solvent of crystallization (1 and 2) both have porous structures, while the two polymorphs (3a and 3b) do not, but all of them can be compared to the structures with phenanthroline. Solution based and mechanochemical syntheses are discussed, as well as the chemical properties of these complexes.



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Keywords: copper(II) complex, crystal structure, solvatomorphism

Discovering new cocrystals via coformer-network analysis

Rene de Gelder¹, Jan-Joris Devogelaer¹, Hugo Meekes¹, Elias Vlieg¹

 Solid State Chemistry, Institute for Molecules and Materials, Radboud University, Nijmegen, Netherlands (Holland, Europe)

email: r.degelder@science.ru.nl

The use of multi-component crystals, such as salts, solvates and cocrystals, is an effective way of optimizing the physicochemical and biopharmaceutical properties of active pharmaceutical ingredients (APIs) without modifying the chemical nature of the APIs [1]. Since most APIs are produced in the form of racemic mixtures, the formation of multi-component crystals may also lead to purification of the enantiomers [2]. Therefore, knowledge of the solid-state landscape of an API, in terms of polymorphism and multi-component formation, is of paramount importance during the design and optimization of the final drug product.

The experimental screening of new multi-component systems, and specifically cocrystals, is a labor and time intensive job and computational tools to understand and predict new cocrystals can significantly speed up the discovery of new solid forms. In this contribution, we present a data-mining approach that exploits the vast amount of information contained in the Cambridge Structural Database [3] in order to predict new multi-component systems. First, all information on salts, solvates and cocrystals is converted into component networks. Next, the networks are analysed to discover their organizational principles and to find the best algorithm for cocrystal prediction. These algorithms are then used to discover unknown cocrystals on the basis of the coformer network (Figure). The prediction results from this new network approach were validated for both a common coformer and an API, resulting in the discovery of several new cocrystals.



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Keywords: cocrystals, Cambridge Structural Database, networks

MS31-P06

Solid form landscapes and access to polymorphs and solvates of several chlorontrobenzoic acid isomers

Agris Bērziņš¹, Ilva Kresse¹, Estefanija Bogdanova¹, Andris Actiņš¹

1. Faculty of Chemistry, University of Latvia, Riga, Latvia

email: agris.berzins@lu.lv

Five different isomers of chlorontrobenzoic acid -2-chloro-4-nitrobenzoic acid (2C4NBA), 4-chloro-2-nitrobenzoic acid (4C2NBA), 2-chloro-5-nitrobenzoic acid (2C5NBA), 5-chloro-2-nitrobenzoic acid (5C2NBA), and 4-chloro-3-nitrobenzoic acid (4C3NBA) were crystallized from numerous different solvents. The obtained results showed that only 2C4NBA forms more than one polymorph (polymorphs I and II) and a hydrate (these forms have already been reported in previous studies of 2C4NBA [1,2]). Meanwhile, several solvates with organic solvents were obtained for each of the isomer (6 for 4C2NBA and 2C5NBA, 4 for 4C3NBA and 3 for 5C2NBA), although again 2C4N-BA formed the most - 8 (with some already reported [2]). Interestingly, all isomers formed solvate wit N,N-dimethylacetamide and N-methyl-2-pyrrolidone, while all except for 5C2NBA also formed solvates with DMF and DMSO. This observation indicates on tendency of these molecules to crystallize together with amides and sulfoxydes.

Crystal structure analysis of non-solvated forms was used to try to obtain insight into the differences observed for the solid form landscape of chlorontrobenzoic acid isomers. As crystal structures of non-solvated 2C5NBA, 5C2NBA and 4C3NBA were not available, they were determined from the PXRD measurements in capillary.

More detailed study was performed for 2C4NBA. Crystallization experiments of unsolvated 2C4NBA in several different conditions were performed from numerous solvents selected to represent different physicochemical properties. The obtained results clearly showed that the solvent as well as crystallization conditions affect the outcome of the crystallization experiment, although conclusions about the conditions for selective crystallization of polymorph II (less stable form at ambient and elevated temperature) were ambiguous.

Characterization of 2C4NBA monohydrate MH showed that it is not particularly stable. Additionally, crystallization experiments from solvent mixtures with different water activity suggested that the crystallization of MH is kinetically hindered even in conditions where MH is thermodynamically stable. Crystallization 2C4NBA from mixtures of water and solvents forming 2C4NBA solvates (e.g., DMSO, 1,4-dioxane) clearly pointed out that in slow crystallization only the solvate with the respective organic solvent could be obtained even at very high water activity, while MH could only be obtained by fast solvent exchange crystallization using excess amount of water.



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Keywords: Crystallization, Solid form screening, Solid form landscape

MS31-P07

Polymorphism in 2-propyl-1*H*-benzimidazole

Noelia De La Pinta¹, Aurora J. Cruz-Cabeza², TomaszBreczewski³, Xabier M. Aretxabaleta³, Feo. Javier Zuñiga¹, Maria Mar Quesada-Moreno⁴, Juan Ramón Avilès-Moreno⁶, Juan Jesús López-González⁴, Rosa M Claramunt⁶, Jose Elguero⁷

- Dpto. Física Materia Condensada, Fac. de Ciencia y Tecnología, Universidad del País Vasco, Leioa, Spain
- 2. School of Chemical Engineering and Analytical Sciences, The University of Manchester, Manchester, United Kingdom
- Dpto. Física Aplicada II, Fac. de Ciencia y Tecnología, Universidad del País Vasco, Leioa, Spain
- Departamento de Química Física y Analítica, Universidad de Jaén. Campus Las Lagunillas, Jaen, Spain
- Departamento de Sistemas Físicos, Químicos y, Naturales, Universidad Pablo de Olavide, Sevilla, Spain
- Dpto. Química Orgánica y Bio-Orgánica, Fac. de Ciencias, Universidad Nacional de Educación a Distancia (UNED), Madrid, Spain
- Instituto de Química Médica, Centro de Química Orgánica Manuel Lora-Tamayo, CSIC, Madrid, Spain

email: noelia.delapinta@ehu.eus

Benzimidazoles, indazoles and benzotriazoles are important organic molecules very common in biological systems. Besides the role the play in these systems, they have received considerable attention in material sciences because they form materials based on these heterocycles, which exhibit notable conductivity and ferroelectric properties [1].

2-propyl-1H-benzimidazole (2PrBzIm, C10N2H12) [2], is a flexible molecule whose conformers are chiral except in the planar configuration. The compound exhibit polymorphism associated with an irreversible reconstructive-type phase transition at T= 384 K from an ordered structure I $(P2_12_12_1)$ [2] to a new polymorphic form II_{HT} (Pca2₁). The structural transformation between both polymorphs is interpreted by means of changes in packing and the configuration of the hydrogen bonded molecular chains. In addition, the polymorph II_{HT} undergoes two reversible phase transitions, at 361 K to another form II_{RT} with the same space group and at 180 K to a low temperature form II_{1T} doubling one of the cell parameters. The calculation of the conformational energy landscape against the intramolecular torsion angles in 2PrBzIm allows to distinguish between changes and adjustments of the conformational configuration of the molecules in the different structures.



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Keywords: 2-propyl-1H-benzimidazole, polymorphism

MS31-P08

Understanding supramolecular interactions with hydrogen bond propensities

Andrew Maloney¹, Elna Pidcock¹, Richard Sykes¹, Peter Wood¹

1. The Cambridge Crystallographic Data Centre, Cambridge, United Kingdom

email: maloney@ccdc.cam.ac.uk

The variety of supramolecular interactions in the solid state can lead to substantial risk or untold opportunity. Lack of control of such interactions can lead to crystal form polymorphism and can have a critical impact on formulated product robustness, with pharmaceuticals having been withdrawn from the market upon the unexpected appearance of a more stable polymorph. However, a detailed understanding of those same interactions can provide an opportunity to generate materials with desired properties through crystal engineering.

The Cambridge Structural Database contains over 940,000 crystal structures, and data points from many millions of individual supramolecular interactions. We can use this data from every crystal structure ever published to understand the solid form landscape of a novel material. What are the risks of polymorphism, and can we engineer specific packing motifs?

The Hydrogen Bond Propensity method makes use of statistics derived from hydrogen bonds observed in similar crystal structures, along with an understanding of the chemistry of a molecule, to make predictions on the likelihood of forming specific interactions in the solid state.[1] When combined with a knowledge of the coordination environment of the functional groups of that molecule, we can generate a landscape of likely hydrogen bonding networks. [2] By understanding the supramolecular interactions that occur in a crystal structure, we are able to understand the risk of polymorphism resulting from variations in these interactions.

In this presentation, we will describe the Hydrogen Bond Propensity method and its application to understanding polymorphism in the organic solid state. We will highlight improvements that we are making to the method and discuss how it can be applied to the design of novel multi-component systems.[3]

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Keywords: hydrogen bonding, polymorphism, co-crystals

Understanding supramolecular role in mechanochromic luminescent polymorphs

Marcelo Echeverri1, Berta Gomez-Lor1

1. Instituto de Ciencia de Materiales de Madrid, Madrid, Spain

email: m.echeverri@csic.es

Mechanochromic materials (i.e. solids possessing light emitting properties that vary upon mechanical grinding or pressing), arouse much interest in recording or sensing applications that involve luminescent detection. However, only in a few of them an adequate understanding about the origin of the color change has been achieved. Light-emitting single crystalline compounds are especially interesting for allowing correlating the changes in the solid-state luminescent properties with variations in the molecular or supramolecular structure.¹

In the quest for efficient light emitting compounds, benzothiadiazole (BTD) is one of the preferred moieties. This electron deficient heterocycle presents high fluorescence quantum efficiencies and has a strong propensity to adopt quinoid conformations, thus facilitating charge transfer between attached substituents and enabling the tuning of its emission properties.² Herein we present a new BTD-derivatives series, which each one crystallizes in two different polymorphs. These compounds change their light emitting properties due to slight changes of their crystallographic packing, offerings an excellent opportunity to establish optimal supramolecular arrangement for photonic applications.



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Keywords: mechanochromic, luminescent, supramolecular

MS31-P10

Supramolecular synthons: structural features in various crystalline environment

Olga Lodochnikova1

1. Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, Kazan, Russia

email: lod_olga@mail.ru

The key concepts of crystalline engineering are intermolecular interactions and the supramolecular synthons which are formed by such interactions. The so-called "Synthon approach" greatly helps to simplify the understanding and description of crystal structures.

In this work, the structural features of a number of known and new supramolecular synthons in a different crystalline environment are studied. By the structural features we mean the geometric parameters of strong "synthon-forming" non-covalent interactions, the conformation of the synthon and the possibility of its additional stabilization through secondary intermolecular interactions, which may turn out to be different in different crystalline forms. Thus, the influence of the crystal environment on the structure and stability of the synthons that are classic for supramolecular chemistry: carboxyl, amide, thioamide, sulfonamide, and some others, in different polymorphic forms and in "racemate-conglomerate" pairs has been studied. To obtain data on the behavior of synthons in different environments, key series of compounds has been studied for polymorphism and for a tendency to spontaneous resolution of enantiomers

An extremely rare type of polymorphism "conglomerate 1-conglomerate 2" has been discovered ^[1]. In both polymorphs, the main formative motif is a homochiral chain (helix) based on the same supramolecular α -hydroxyamide open-chain synthon that takes different symmetry depending on the crystal system.

For the classical carboxylic acid synthon, the ability to form a stable interaction of the "Lp...synton" type is found, which can cause a significant amplification of synthon-forming hydrogen bonds.

For the known thioamide synthon, the effect of a "chiral-dependent conformational memory" is found - a pairs of thiourea molecules "memorize" their mutual arrangement both in the hetero- and homochiral H-bound dimers and reproduce it in the structure of metal complexes corresponding to them by stereochemistry.

The possibility of transferring an amide open-chain supramolecular synthon, which is symmetrical relatively to the glide plane in the crystals of isonyazide dervatives, from the racemic medium into the homochiral one has been discovered ^[2]. It was achieved by inclusion of a second independent molecule into a cell.

A new tetrameric cyclic sulfinamide synthon has been found, the formation of which is accompanied by the formation of an H-bound tetramer with a sofisticated stereochemical construction.

A new cyclic centrosymmetric β -hydroxysulfoxide synthon, capable of self-assembly in both the racemic and homochiral medium, has two stable conformations realized in the room temperature and low-temperature phases^[3]. This work was financially supported by the Russian Science Foundation (grant No 17-13-01209).

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Keywords: supramolecular synthon, polymorphism, intermolecular interactions

MS31-P11

Combining crystal structure prediction and structural comparison with experimental screening: a potential route to more polymorphs, including a 2-for-theprice-of-1 special

Riccardo Montis1, Michael Hursthouse2, John Kendrick3

- School of Chemical Engineering and Analytical Science The University of Manchester, Manchester, United Kingdom
- 2. Chemistry University of Southampton, Southampton, United Kingdom
- Department of Chemistry and Forensic Science University of Bradford, Bradford, United Kingdom

email: riccardo.montis@manchester.ac.uk

Although our current knowledge on polymorphism has been advancing significantly in recent years, this fascinating topic still represents a challenging aspect of structural crystallography and solid-state chemistry. Despite the major enhancements in experimental and computational methods, the highly successful computational studies invariably predict far more feasible structures than are experimentally found, even when further extensive experimental screenings are made. Possible reasons for this discrepancy have been previously suggested but still questions such as *Why don't we find more polymorphs?* remain open.¹

In this work we explore the idea that detailed comparative analyses of predicted and experimental polymorphs may represent a further useful tool for polymorph screening. The identification of structural similarities and differences might help in discriminating which structure, within the crystal energy landscape, would seem likely to be experimentally isolated.² This information might be also used to identify whether pairs or groups of structures are so closely related that they may convert one into the other, during the nucleation/crystal growth stages or by proper solid-solid phase transitions, preventing the observation of some potential metastable forms. To follow these objectives, we compared experimental and predicted structures from the previous results of a CSP study by Asmadi et al.³ on a group of three rigid, planar small molecules of known crystal structures, 2-methyl-, 3-methyl- and 2,3-dimethyl-benzo[b]thiophene 1,1-dioxide.

The results of the crystal structure comparison of the ten lowest energy predictions from the CSP calculations for each derivative with the known, unique experimental crystal structures are discussed. A short experimental screening leading to the discovery of three new polymorphs is also presented.

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Keywords: Polymorphism,

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Liquid essential oils tamed in the solid forms by cocrystalizzation: from the design to the industrial application

Paolo Mazzeo¹, Claudia Carraro¹, Silvia Agazzi¹, Federica Bianchi¹, Alessia Bacchi¹

 Dipartimento di Chimica, della Vita e della sostenibilità ambientale, University of Parma, Parma, Italy

email: paolopio.mazzeo@unipr.it

Co-crystals are multicomponent crystalline materials in which different molecular entities are stoichiometrically kept together within the same crystal lattice. Their properties are a blend of single component characteristics, tuned by internal interactions. In modern times, cocrystals are of great interest in the pharmaceutical context because they are able to modify the chemo-physical properties of the pure drug by appropriate selecting a suitable coformer. However, some important molecules for human health are liquid at room temperature, which may influence the efficacy of their formulation since they tend to be less stable than solid forms. For this reason, the stabilization of liquid APIs is of enormous interest not only for the final delivery of the drug product but also for its storage, transportation and handling. Within this project we address the problem of taming liquid essential oils (EOs) in crystalline forms at ambient conditions and assess their applicability in the agro-food industrial arena. In addition to their widespread use as flavouring agents, EOs represent a "green" alternative in pharmaceutical, nutritional and agricultural fields due to their reported antimicrobial, antimycotic and antioxidant properties. The use of EOs in industrial context is anyhow limited by their low-melting point, which negatively affects their chemical stability. As proof of concept, we here successfully forced the enthalpic stabilization of EOs, such as eugenol (a major component of clove oil), carvacrol (extracted from the oregano essential oil) and thymol (present in the oil of thyme) by providing a new efficient intermolecular network in the solid state, co-crystallizing them with different N-based coformers. Coformers were appropriately chosen among a list of regulated substances apt for agro-food industries.

All products have been fully characterized and their properties – i.e. solubility and EOs release in air and in simulant media – described in relation to their three-dimensional structure with particular emphasis on the role of the coformer used.

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Keywords: Cocrystals, Essential-oils, Crystal-Engineering

MS31-P13

Insights into Weak C-H...F-C Interactions in C_6F_6 : $C_6H_{6-n}Me_n$ co-crystals using a combination of powder neutron and X-ray diffraction, single-crystal diffraction, and DSC

Jeremy Karl Cockcroft1

1. Department of Chemistry, University College London (UCL), London, United Kingdom

email: j.k.cockcroft@ucl.ac.uk

Powder X-ray and neutron diffraction (PXRD and PND) are ideal tools for the study of solid-solid phase transitions, especially when complemented by DSC measurements. Similarly, single-crystal X-ray diffraction (SXD) is the method of choice for structure determination, especially given the capabilities of modern X-ray equipment (focussed micro-source X-rays with 2D detectors) combined with state-of-the-art data processing (CrysAlisPro) and analysis (Olex2) software. In addition, variable temperature (VT) crystallography can provide a more detailed understanding of the interactions between molecules than the static oneshot single temperature approach. Combining all of these methods has improved our understanding of the co-crystal system $C_6F_6:C_6H_{e-m}Me_n$ for n=0 to 3.

The structure of phase IV of the prototype material C6F6:C6H6 was solved from combined neutron and synchrotron X-ray powder diffraction a quarter of a century ago^[1], but a detailed understanding of the other 3 phases has remained elusive until now: new laboratory PXRD and SXD data has resulted in the determination of the crystal structures of the unknown phases and a better understanding of the transitions, particularly when combined with DSC measurements^[2]. Furthermore, due to the combined use of PXRD, DSC and SXD techniques, the origins of the phase transitions in the related system C6F6:C6H3Me3 co-crystal system have now been fully understood^[3]. More recent studies of C₆F₆:C₆H₄Me₂(p-xylene) using a similar approach has reveal subtleties in the structure of this adduct as a function of temperature which have not previously been seen; it exhibits similarities in structural behaviour to that of the C₆F₆:C₆H₃Me₃ adduct. Finally, a preliminary PXRD study combined with low temperature DSC on C6F6:C6H5Me (toluene) shows that this system is more similar to the prototype material. In each case, an understanding of the changes in symmetry as a function of temperature is essential to solving the structures.

Variable temperature crystallography provides a tool for studying the competing intermolecular interactions in these systems. In all cases, there is a very strong electrostatic interaction from the equal and opposite quadrupolar force between the C_6F_6 and $C_6H_{6-n}Me_n$ rings leading to columns of molecules stacked like dinner plates, but subtle changes in the C-H...F-C interactions between columns of molecules as a function of temperature lead to a variety of phase transformations.

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Keywords: Variable temperature powder diffraction, C-H...F-C Interactions, Co-crystals

MS31-P14

Co-crystallisation of energetic materials with reduced sensitivity

Nilgun Sen1, Colin R. Pulham1

1. University of Edinburgh/Chemistry, Edinburgh, United Kingdom

email: nilgunsen2001@gmail.com

Insensitive explosives have attracted significant interest in the past three decades owing to their potential application in numerous energetic materials. Research of the explosive of low impact sensitivity and high explosive performance is the vital problem in the energetic materials, which has not been solved yet (1-4). Efforts have been made to diminish this through synthesis of new molecules, however this is usually a complex, need to time consuming process cost-effective production methods, extensive validation, and requirements to meet increasing challenging performance target (5). Co-crystallisation is new an effective technique to improve the solubility, bioavailability physical and chemical stability properties of drugs without altering their chemical structure, and it is extensively used for the pharmaceutical industry (6-9). Therefore, co-crystallization may supply a new method to possibility of tuning the performance and sensitivity of an energetic material without requiring complex preparation or synthesis of novel compounds (10-13). To modify and improve the properties of energetic materials, via co-crystallisation between TNT, Picric Acid with non-energetic materials were studied. Co-crystallisation studies including characterization (single crystal X-ray data, Powder X Ray diffraction), thermal behavior (Differential Scanning Calorimetry), impact sensitivity (BAM Fall Hammer), and intermolecular interactions were carried out in detail. And also we analysed the crystal packing and show how this may influence sensitivity to impact.

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Keywords: Sensitivity,Inter molecular interaction, Cocrystallisation

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Steroids as coformers in cocrystallization of PAHs and heterocycles

Filip Topić 1, Davin Tan1, Tomislav Friščić1

1. Department of Chemistry, McGill University, Montreal, Canada

email: filip.topic@mcgill.ca

Currently, function and biological behaviour of steroids are believed to be mainly determined by terminal chemical groups attached to their backbone. Recently, however, mechanochemical solid-state screening techniques developed by our group revealed there may be another way for steroids to recognize and bind other molecules, named the $\alpha \cdots \pi$ interaction, so far observed in solid-state complexes of the steroid sex hormone progesterone with electron-rich, planar aromatic molecules (arenes).[1] This interaction takes place specifically between one side of the progesterone molecule, known as the α -face, and the π -electron cloud above the plane of the aromatic molecule. Importantly, the small number of other steroids explored so far suggest that such supramolecular assembly is highly dependent on the fine detail of the steroid backbone,[1,2] thus paralleling their behaviour in biological systems, where small differences in steroid structures are immediately reflected in their biological activities. In the context of supramolecular chemistry, the assembly by $\alpha \cdots \pi$ interaction can enable the rational design of new solid-state materials with potential use in drug delivery.

We set out to explore the limits of the cocrystallization strategy with progesterone, using larger PAHs such as perylene and coronene, and polyaromatic heterocycles such as phenanthridine, phenanthroline and others. The cocrystal screening was conducted mechanochemically, i.e. by liquid-assisted grinding, and the successful formation of a cocrystal established by powder X-ray diffraction and ATR-IR spectroscopy. A number of cocrystals were successfully obtained and their structures determined by single-crystal X-ray diffraction.

Our results so far demonstrate impressive reliability of the $\alpha \cdots \pi$ interaction, witnessed by a relatively high rate of successful cocrystallization within the investigated coformers. On the other hand, the stoichiometry of the cocrystals could so far not be accurately predicted in all cases, with all of 1:1, 2:1 and 3:1 steroid-to-coformer stoichiometries observed.



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Keywords: steroid, arene, cocrystal

Access to several crystalline forms of R-encenicline hydrochloride using desolvation of various solvates

Artis Kons¹, Andris Actiņš¹

1. Faculty of Chemistry, University of Latvia, Riga, Latvia

email: artis.kons@lu.lv

R-Encenicline (N-[(3R)-1-azabicyclo[2.2.2]oct-3-yl]-7chloro-1-benzothiophene-2-carboxamide) hydrochloride (Enc-HCI) is a partial, selective agonist of the α -7 nicotinic acetylcholine receptor. It is being developed for the treatment of cognitive deficits in schizophrenia and Alzheimer's disease. Previously, three monohydrates (I, II and X) were reported in the patent [1], recently we reported fourth polymorph of Enc-HCI monohydrate (III) as well as four dehydrates of all monohydrates (I_D, I_D and II_D) [2].

The solid state landscape of Enc-HCl presents several more nonsolvated polymorphic forms as well as large number of solvates. Almost all of these polymorphic forms (V, VI,VII,VIII,IX) can only be obtained by means of desolvation of different solvates. Moreover, depending on the different desolvation conditions two different polymorphs can be obtained from the same acetic acid disolvate (S_{AA}). Indeed, when the desolvation process is performed in elevated temperature - polymorph VIII is produced, but in dry gas flow - polymorph IX. The only polymorph that is accessible without the parent solvated phase is form IV.

The crystal structures of six polymorphs as well as their precursors have been determined directly from powder diffraction data. The crystal structures of precursors were found to be relatively structurally similar and related to those of desolvated phases, which was consistent with the observed phase transitions among the related pairs. In addition, a comparison of the thermodynamic stability of polymorphs were performed using DFT calculations, differential scanning calorimetry data and solvent mediated slurry-bridging experiments.

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Keywords: encenicline, polymorphs, solvates

MS31-P17

Multicomponent crystals of sulfapyridine and sulfadiazine

Nikoletta B Bathori1, Kelly Nzwanai Shunje1, Elise JC de Vries1

1. Chemistry Department, Cape Peninsula University of Technology, Cape Town, South Africa

email: bathorin@cput.ac.za

Crystal engineering principles were used to cocrystallise sulfa drugs, sulfapyridine (SFP) and sulfadiazine (SFD), with aromatic acids and an amine via solution crystallisation. Sulfapyridine formed cocrystals with 3-nitrobenzoic acid (SFP·3NBA), 5-bromosalicylic acid (SFP·5BSA), 4-dimethylaminopyridine (SFP·4DMAP) and salts with 4-nitrobenzoic acid [SFP'][4NBA⁻], 3,5-dinitrosalicylic acid [SFP⁺][DNSA⁻] and 3,5-dibromosalicylic acid [SFP⁺] [DBSA⁻], while sulfadiazine formed a salt with 3,5-dinitrosalicylic acid [SFD⁺][DNSA⁻].

The SFP and SFD compounds exhibit tautomerism. In this work it was investigated how the introduction of coformers with varying acidity provides the possibility to form a variety of synthons, and therefore disrupt the common preferred interactions within the sulfonamides. Using selected acids as coformers, the effect on crystal packing of the coformer's substituent position was examined by using the isomers 3NBA and 4NBA. 5BSA and DBSA were employed to analyse the effect of the number of substituents on hydrogen bond formation and crystal packing. In addition, it was investigated how small structural changes in the pharmaceutical compound influences the crystal packing by cocrystallising structurally similar SFP and SFD with the same coformer. Evaluation of the change in coformer acidity was studied by using a pyridine coformer, 4DMAP, and its crystal packing was analysed and compared to structures formed with carboxylic acid coformers.

Finally, we examined how inter-conversion of tautomers promotes crystal formation by conforming to the geometric demands of the different coformers.

Keywords: sulfadrugs, tautomers, cocrystals

Computional studies of droperidol / benperidol solid solution phase formation.

Elīna Sala1, Agris Bērziņš1, Kristaps Saršūns1

1. Faculty of Chemistry + University of Latvia, Riga, Latvia

email: eliina.sala@gmail.com

Goal of the research is to rationalize and find one common ground how to predict formation of solid solutions between chemically similar molecules and how to explain formation or absence of mentioned phase (structural and energy aspects).

Experimentally it is confirmed that several of the chemically similar benperidol and droperidol solvates yield solid solutions with limited solubility [1], however there is lack of insight on theoretical studies, since solid solutions if one of the least researched solid phase. The analysis of crystal structures have been accompanied for a while with various computational techniques – for instance with calculations of total unit cell energy we can explain why one structure is more favourable, it is possible to simulate solid solutions with various compositions and find limitations for compound solubility in each other by comparing total unit cell energy, as well as simulated structures allow to compare bond angles and lengths.

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Keywords: computional chemistry, solid solution

MS32- Molecular recognition and crystal engineering

Chairs: Dr. Berta Gómez-Lor, Prof. Delia Haynes

MS32-P01

Structure and conformation of photosynthetic pigments and related compounds

Dáire Gibbons1, Keith J. Flanagan1, Mathias O. Senge1

1. Trinity College Dublin, Dublin, Ireland

email: dairegibbons0@gmail.com

Normal-coordinate Structural Decomposition (NSD) has been used to study the role of distortions of tetrapyrroles in biochemical mechanisms.^[1] In the Senge group, NSD has been used to determine the extent that different modes of distortions contribute in 3D structures of similar but distinct porphyrinoid macrocycles.[2] In this project we are intending to conduct a detailed comparative analysis of chlorophyll related molecules at a small molecule, high resolution level. Additionally, we will also establish how effective the NSD is by determining specific 3D features of porphyrins, chlorins, and their metal derivatives. With this in mind we used the Cambridge Structural Database^[3] to obtain the X-ray crystal structures of free base 5,10,15,20-tetraphenylporphyrins (TPP); free base 2,3,7,8,12,13,17,18-octaethylporphyrins (OEP); free base porphyrins with increasing β-substituted ethyl groups (XETPP) (X = 0-8); free base chlorins with increasing β -substituted ethyl groups (XETPC) (X = 0-8) and the Zn(II) derivatives of the four groups mentioned above. The NSD of these compounds were then obtained using the NSDGUI developed by Shelnutt and co-workers.[4]

Chlorophylls and porphyrins have been shown to exhibit a wide range of different macrocycle conformations. These can occur by metalation, steric effects of peripheral or axial ligands, N-substitution, protonation, and π -aggregation in the environment. The compounds listed above were discussed in terms of their out-of-plane (oop) and in-plane (ip) distortion modes. In the TPPs, the main oop distortion mode is wav(x). In OEPs, the main oop mode is wav(y). Factors such as solvent, axial ligands, and π -interactions influence the 3D structure of these compounds, resulting in a comprehensive preference for each distortion mode based off interactions. OKOQUA (OEP) is solvated with a tetracvanoquinodimethane solvent that approximately triples the wav(x) distortion mode compared to the non-solvated OEP. Increasing the number of ethyl chains on the β carbons in the XETPPs increases the oop distortion, which is clearly seen in the sad distortion. In the XETPCs (X = 2), increases of roughly 1.0 Å exist in the sad mode compared to corresponding porphyrins. When X = 4(cis), decreases in distortion occur when ethyl chains are on the reduced pyrrole and increases are observed when ethyl chains are on the non-reduced pyrrole. The insertion of a Zn(II) results in a wav(x) decrease in TPP of 0.1 Å. This can be rationalized by the N-Zn(II) bond which contracts the porphyrin core. Additionally, it should be noted that peripheral substitutions have a larger impact on 3D structure than Zn(II) metal insertions. This is mainly seen in the difference between *sad*, *ruf* and *dom* distortions in XETPPs and XETPCs. From the results obtained in this test case, we can now go on and use these observations to discuss the macrocycle conformations in chlorophyll.



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Keywords: NSD, chlorophyll, porphyrins

MS32-P02

Crystal structure investigation for series of salts of 2me-5na with different acids

Volodymyr Medviediev1, Marek Daszkiewicz1

1. Division of Structure Research, Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wroclaw, Poland

email: v.medvedev@int.pan.wroc.pl

The many of nitroaniline derivatives are materials with nonlinear optical (NLO) properties [1]. The molecules of nitroanilines contain the amino group which can be protonated and new compounds can be obtained in acidic conditions. Therefore, a search of compounds with NLO properties can be expanded for a large group of organic ionic compounds. Previously, some complexes of 2-methyl-4-nitroaniline with inorganic acids were studied [2]. As a continuation of those studies, here we present crystal structure of six new salts of 2-methyl-5-nitroaniline (2Me-5NA) with inorganic acids.

Five of obtained crystals have centrosymmetric space groups, but one does not have the centre of symmetry. Structures of all the compounds are stabilized by N–H+++A hydrogen bonds between $-NH_3^+$ group and inorganic anion. The stability of all the salts was checked in the rage 295-100K and no phase transitions were revealed.

Fig. 1. The networks of hydrogen bonds in crystal structures of $(H-2Me-5NA)HSO_4$, (H-2Me-5NA)Br and $(H-2Me-5NA)NO_3$ at 295K.



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Keywords: Nitroanilines, NLO, structure

The impact of stereogenic center on the architecture of the water framework: 2-methylpyrrolidine and *sec*-butylamine hydrates

Patryk Rzepiński¹, Łukasz Dobrzycki¹, Michał Cyrański¹, Roland Boese¹

1. Chemistry Department, University of Warsaw, Warsaw, Poland

email: przepinski@chem.uw.edu.pl

sec-Butylamine and 2-methylpryrrolidine are primary aliphatic and secondary cyclic amines, respectively. They can exist in enantiopure form or as a racemic mixture. In both cases they can interact with water molecules forming hydrates of rather differentiated architecture. Their analyses shed light on the influence of stereogenic center on crystal packing and, in consequence, on the transfer of chirality to water frameworks and on their complexity.

Using the in situ crystallization technique [1] assisted by IR laser focused radiation we were able to obtain crystals of racemic amines, (R)-2-methylpyrrolidine and (S)-sec-butylamine. For each case we obtained also hydrates. As expected, racemic 2-methylpyrrolidine or sec-butylamine crystallize in centrosymmetric group (monoclinic P21/n or orthorhombic Pccn, respectively), whereas (R)-2-methylpyrrolidine and (S)-sec-butylamine in non-centrosymmetric ones $(P2_1, \text{ or } P2_12_12, \text{ respectively})$. In the case of hydrates the amine molecules are incorporated to 3D water network. Racemic mixture and R isomer of 2-methylpyrrolidine lead to 7 hydrate but they differ in crystallographic systems $(P2_1/n \text{ or } P2_12_12_1, \text{ respectively})$. The case of sec-butylamine is different because the presence of stereogenic center dramatically changes the symmetry. Racemic mixture of sec-butylamine and water leads to $7^{1/3}$ hydrate (P2₁/c space group) while the mixture of S isomer and water gives 6 hydrate ($P2_12_12_1$ space group).

It is worth to mention that hydrogen atoms for 2-methylpyrrolidine hydrate (both racemic and enantiopure) are ordered whereas in the case of *sec*-butylamine hydrate they are disordered.

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Keywords: chirality, hydrates, in situ crystallization

MS32-P04

Porous supramolecular architectures based on π -stacking interactions between discrete metal-adenine entities and theobromine/ caffeine methylxanthines

Jon Pascual Colino¹, Maite Perfecto-Irigaray¹, Garikoitz Beobide Pacheco¹, Oscar Castillo Garcia¹, Antonio Luque Arrebola¹, Sonia Pérez-Yañez¹

1. Department of Inorganic Chemistry, University of the Basque Country, UPV/EHU, 01006 Vitoria-Gasteiz, Spain

email: jonpascu2@gmail.com

Taking into account the great potential of MOFs, this work is focused on a relatively recent new class of analogous porous materials in which coordination bonds are released from guiding the crystal structure and supramolecular interactions play this role.1 Herein we present the results obtained for π - π stacking interactions as the driving force to develop porous supramolecular metal-organic frameworks (SMOFs) as an alternative to more directional hydrogen bonding interactions. In particular, the use of adenine and methylxanthines has given rise to several compounds presented in this communication. The blue compound $[Cu_7(\mu-ade)_6(\mu_3 OH_{6}(\mu-H_{2}O)_{6}$ (theo)₂ · 28H₂O (1) (ade: adeninato, theo: theobrominato) is formed by wheel-shaped cationic units where the Cu(II) atoms are bridged by hydroxide anions, water molecules, and adeninato ligands with a m-kN3:kN9 coordination mode. The supramolecular assembly (Figure 1) takes place mainly through π - π stacking interactions involving the adeninato ligands of the rigid heptameric entities and theobrominate moieties. Compound 1 exhibits an open-framework with voids representing 37% of the unit cell volume, but the plasticity of the π - π interactions causes a reversible shrinkage of the porous system upon activation that precludes the adsorption of gas molecules.

Dark purple compounds [Cu₂(µ-ade)₄(H₂O)₂]·3Htheo 7H₂O (2), [Cu₂(µ-ade)₄(H₂O)₂] 2Htheo 18H₂O (3) and $[Cu_2(\mu-ade)_4(H_2O)_2]$ (caf) ~6H₂O (4) (Htheo: theobromine, caf: caffeine) contain neutral windmill units in which two copper atoms are bridged by four m-KN3:KN9 adeninato ligands. Their crystal structures highly depend on the supramolecular interactions of the theobromine and caffeine bases. In compound 2, two theobromine molecules are hydrogen bonded to the Hoogsteen face of two trans-arranged adeninato ligands, whereas a third theobromine molecule is joined to the Watson-Crick face of one of the previous adeninato ligand. In compound 3, with a lower amount of theobromine, the Watson-Crick interaction is not present. In both compounds, the 3D crystal structure requires the additional presence of π - π stacks between the theobromine molecules.

In compound 4, as the methyl groups of the caffeine molecule do not allow hydrogen bond interactions, the adeninato ligands are hydrogen bonded among them to generate, together with π -stacking interactions, supramolecular sheets containing rectangular windows in which the caffeine molecules are located. Only compound 4 showed permanent porosity, adsorbing a significant amount of CO₂ (0.88 mmol of CO₂/g at 5 bar and 273 K). The magnetic characterization of the compounds indicate a ferromagnetic behaviour for ${\bf 1}$ and strong intradimeric antiferromagnetic interactions in compounds ${\bf 2}$ and ${\bf 4}.$



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Keywords: SMOFs, supramolecular interactions, π - π stacking

MS32-P06

Temperature-dependent supramolecular isomerism of lutetium-aminoterephthalate metal-organic frameworks: synthesis, crystallography and physical properties

Alla Dikhtiarenko¹, Pablo Serra-Crespo², Sonia Castellanos³, Alexey Pustovarenko⁴, Rafael Mendoza-Meroño⁵, Santiago García-Granda⁵, Jorge Gascon¹

- 1. Kaust Catalysis Center, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia
- Radiation and Isotopes for Health, Department of Radiation Science and Technology, Faculty of Applied Sciences, Technical University Delft, Delft, Netherlands (Holland, Europe)
- Advanced Research Center for Nanolithography, Amsterdam, Netherlands (Holland, Europe)
- Chemical Engineering Department, Delft University of Technology, Delft, Netherlands (Holland, Europe)
- 5. Departamento de Química Física y Analítica, Universidad de Oviedo, Oviedo, Spain

email: alla.dikhtiarenko@kaust.edu.sa

Polymorphism or supramolecular isomerism is becoming an increasingly important subject in the field of crystal engineering, as it may facilitate the design of porous polymeric materials with targeted physical properties.[1] In this context, the unique properties of MOF polymorphs, displaying both different crystal structures and identical molecular composition, allow for the derivation of structure-property relationships solely based on structural parameters or topology of the polymeric network. There are various key factors governing the formation of MOFs' polymorphic forms, including reaction time, temperature, concentration of precursors, pH, solvent, modulators, and so on. Although numerous individual factors^[2] or their conjunction^[3] affect the occurrence of polymorphic forms, temperature is the one of the most important variables. The study of polymorphism is not only important in producing novel materials with target properties but may also be helpful in developing a fundamental understanding of the factors influencing crystal growth, such as reaction temperature.

In this line, we present the investigation on the relationship between the crystal structures and gas adsorption / fluorescence properties of lutetium(III) 2-aminoterephthalate MOFs isomorph series. Three supramolecular isomers of lutetium metal-organic framework, $\{Lu_2(H_2O)_4(ATA)_2, 4H_2O\}$ $(Lu-ATA@RT), \{Lu_2(H_2O)_2(C_3H_7NO)_2(ATA)_3\}_n$ (Lu-ATA@100) and $\{Lu_2(C_3H_7NO)(ATA)_3\}_n$ (Lu-ATA@150), have been obtained from the reaction of Lu(NO₃)₃·6H₂O with 2-aminoterephthalic acid (ATA) at different temperatures. The resulting structures of Lu-ATA MOFs depend on the temperature applied during the synthesis, revealing a temperature-susceptible supramolecular isomerism. Single-crystal X-ray diffraction analyses suggest that new compounds with formula $\{Lu_2(S)_x(ATA)_3\}_n$ (S = solvent: H₂O, DMF) display different three-dimensional architectures which consist on dinuclear lutetium building units. The supramolecular isomer Lu-ATA@RT, formed at room temperature, has a pcu-net topology while its double interpenetrated analogue, Lu-ATA@100, assembles at 100 °C under hydrothermal conditions. Hydrothermal synthesis at 150 °C affords formation of the dense Lu-ATA@150 cagelike framework displaying a new hexagonal-packed net topology. All Lu-ATA isomeric phases are porous and display different gas-uptake behaviour towards carbon dioxide as a function of polymeric network arrangement. The luminescent properties of Lu-ATA frameworks in solid state as well as in suspension in the presence of different solvents reveal a solvent dependent emission.

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Keywords: metal-organic frameworks, supramolecular isomerism, luminescence

MS32-P07

Nanosheets of non-layered aluminium metal-organic frameworks through a surfactant-assisted method

Alexey Pustovarenko¹, Maarten G. Goesten², Sumit Sachdeva³, Zakariae Amghouz⁴, Alla Dikhtiarenko¹, Ernst J. R. Sudhölter³, Freek Kapteijn ³, Beatriz Seoane⁵, Jorge Gascon¹

- 1. Kaust Catalysis Center, King Abdullah University of Science and Technology, Thuwal, Saudi Arabia
- Department of Chemistry and Chemical Biology, Cornell University, Cornell, United States of America
- Department of Chemical Engineering, Delft University of Technology, Delft, Netherlands (Holland, Europe)
- Department of Materials Science and Metallurgical Engineering, Polytechnic School of Engineering, University of Oviedo, Gijón, Spain
- Debye Institute for Nanomaterials Science, Utrecht University, Utrecht, Netherlands (Holland, Europe)

email: oleksii.pustovarenko@kaust.edu.sa

During the last decade, the synthesis and application of metal-organic framework (MOF) nanosheets has received growing interest,^[1] showing unique performances for different technological applications.^[2] Despite the advances reported, the applicability of the synthetic methods developed so far is mainly restricted to MOFs possessing a layered structure. These MOFs consist of stacked 2D layers, being more prone to the formation of nanosheets. However, this subfamily of compounds only embodies a small fraction of the MOF structures reported to date, severely limiting the potential of this promising type of 2D nanomaterials. To the best of our knowledge, only one very recent example has been reported so far on the top-down exfoliation of 3D MOFs.^[3] However, top-down approaches are often associated with particle fragmentation and re-aggregation of the detached sheets. A bottom-up approach for the synthesis of 3D MOF has never been reported.

Within this context, we present a bottom-up surfactant-assisted synthetic approach for the fabrication of free-standing nanosheets of various non-layered 3D Al-containing MOFs, broadening the scope of MOF nanosheets application. Surfactant-assisted pre-organization of the metallic precursor prior to MOF synthesis allows for the manufacture of non-layered Al-containing MOF lamellae. These MOF nanosheets are shown to exhibit a superior performance over other crystal morphologies for both chemical sensing and gas separation. Gas separation behaviour of MOF nanosheets embedded in polymer matrix was explored for CO₂/CH₄ mixture and compared to the nanoparticle-containing composite. The NH2-MIL-53(Al) nanolamellae/ Matrimid® mixed matrix membrane showed a 10-fold increase in CO₂ permeability along with a doubled selectivity in the separation of CO₂/CH₄ mixtures. Moreover, sensing studies on NH2-MIL-53(Al) nanolamellae-coated device suggested the enhanced sensing performance towards different types of alcohols. As revealed by electron microscopy and diffraction, this superior performance arises from the shorter diffusion pathway in MOF nanosheets, whose one-dimensional channels are oriented along the shortest particle dimension.

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Keywords: MOF nanolamellae, chemical sensing, molecular recognition

MS32-P08

Pharmaceutical salts of antidiabetic drugs: mechanochemical synthesis, solid state characterization and solubility evaluation

Duane Choquesillo-Lazarte¹, Cristóbal Verdugo-Escamilla ¹, Argoitz Calvo-Borika², Raquel Fernández-Penas¹, Antonio Rodríguez-Diéguez²

- 1. Laboratorio de Estudios Cristalográficos, IACT, CSIC-UGR, Granada, Spain
- Departamento de Química Inorgánica, Facultad de Ciencias, UGR, Granada, Spain

email: duane.choquesillo@csic.es

The interest in multicomponent solid forms has increased in the last years within the pharmaceutical industry and also the solid-state community due to the possibility of obtaining materials with improved properties^{1,2}. Crystallization strategies, supported by solvent- and solid-based³ techniques, have also received attention in the search and development of efficient methodologies for the screening of multicomponent crystals.

In this work, two antidiabetic drugs with limited aqueous solubility, chlorpropamide and tolbutamide, were selected to develop multicomponent forms on the basis of the synthon types using a series of coformers. Liquid Assisted Grinding (LAG) was used as a mechanochemical synthetic tool. Attempts to produce salts by LAG led to the formation of polycrystalline material. These solids were then characterized by powder X-ray diffraction as well as by spectroscopic and thermal methods. Recrystallization by slow solvent evaporation was carried out when the above-referred techniques strongly suggest the formation of a new solid form. In those cases where suitable crystals were obtained, single crystal X-ray diffraction experiments were performed. Solubility determination of the selected solid forms has proved the advantage they offer over their corresponding parent APIs.

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Keywords: antidiabetic drugs, multicomponent crystals, liquidassisted grinding

Combining crystal engineering strategies in the search for non-centrosymmetric single-crystal structures

Jasper Van de Velde1, Frank Blockhuys

1. University of Antwerp - Department of Chemistry, Antwerp, Belgium

email: jasper.vandevelde@uantwerpen.be

Despite the simplicity and robustness of inorganic NLO materials, their organic counterparts have been attracting attention due not only to their superior NLO performance but also to their faster electronic response and higher thermal stability [1]. The greatest advantage, though, at least from a chemical point of view, is the ability to design both the molecular and supramolecular structure in function of the desired properties or applications [2]. In the case of (lowest-order) single-component NLO materials, the main challenge consists of achieving non-centrosymmetry in the crystal lattice, which is a strict requirement to observe the desired optical effects.

Our previous work on organic optical materials focused on 1,4-distyrylbenzene (1,4-DSB) derivatives with a wide variety of acceptor and donor substituents on the backbone. Such push-pull (A-\pi-D) compounds did yield non-centrosymmetric crystal structures, but the fraction of polar supramolecular structures remains low [3].

In order to maximize the probability for non-centrosymmetry, we now focus on 1,3-DSBs. This idea is supported by an analysis of the Cambridge Structural Database (CSD), which leads to the conclusion that compounds based on 1,3-DSB crystallize non-centrosymmetrically in 25% of the cases, compared to 8% and 11% for 1,4- and 1,2-DSBs respectively. Hence, for any system deviating enough from the typical rigid-rod shape of 1.4-DSBs, but not too much (1,2-DSBs), a higher probability for non-centrosymmetry can be expected. A large-scale quantum chemical screening of molecular 1.3-DSB based structures, in which hyperpolarizibilities, dipole moments and conformational energy differences were calculated, shows that next to $A-\pi$ -D all-carbon scaffolds, also D-n-D systems containing heterocyclic rings and nitrogen atoms in the spacers, can be of value not only in terms of NLO-properties but also in the light of the resulting supramolecular structure. As a result four crystal engineering strategies have been combined in an overall rational design: (1) the formation of an anti-parallel stacking should be hampered by the introduction of lateral steric hindrance between the constituent molecules (1,3-DSBs), (2) the electronic ground-state dipole moment of the constituent molecules should be sufficiently small (D- π -D), (3) the deviation from planarity of the constituent molecules should be increased (nitrogen-containing spacers) and (4) the most favorable conformation of the molecule in the light of strategies (1) and (2) should have an as high as possible energetic advantage with respect to other conformations.

A first series of 1,3-DSBs and 2,5-distyrylheteroarenes is crystallized and characterized with single-crystal X-ray diffraction in order to evaluate these strategies.

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Keywords: nonlinear-optics, crystal engineering, polar crystals

A systematic structural study of halogenated 2-phenylbenzimidazoles

Laura Nagyné Bereczki¹, Zita Makó², Dániel Fegyverneki¹, Nóra Veronika May¹, Tibor Soós¹, Petra Bombicz¹

- 1. Research Centre for Natural Sciences, Hungarian Academy of Sciences, Buadpest, Hungary
- Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Budapest, Hungary

email: nagyne.bereczki.laura@ttk.mta.hu

The tunable interaction strength and the pronounced directionality make halogen bonding an eligible tool for crystal engineering. Due to the polarizability of the halogens, both nucleophilic and electrophilic regions can be found on the surface of covalently bound halogen atoms which allows them to form a variety of secondary interactions in the solid state¹. The interaction strength scales with the polarizability of the halogen atom in a relatively wide range.

The main objective of this study is to determine how and to what extent the type and the position of the halogen substituent may affect the crystal structure if the other influencing factors are reduced as far as possible.

The crystal structures of halogenated 2-phenlybenzimidazoles are compared. The 2-phenylbenzimidazoles are substituted on the phenyl ring in ortho, meta and para positions or simultaneously in two different positions by fluorine, chlorine and bromine. In the studied crystal structures, the halogens form R-X...X-R' and R-X...Pi type halogen bonds and R-H...X-R' hydrogen bonds.

8 structures from the CSD (JEYTUD, MINHOI, TUDXIB, LUJWIW01, DETKIX, GOLNOM, QERTIR, SEZNUH) and 3 new halogenated 2-phenylbenzimidazole structures are compared and analyzed. Correlations between the halogen atom positions, secondary interactions and crystallographic parameters are analyzed by statistical methods.

2-Phenylbenzimidazole has a rigid structure that can be twisted around the benzimidazole-phenyl axis. The solid state interactions of halogenated 2-phenylbenzimidazoles are relatively simple which makes them good model compounds for this type of study. Their structure is basically determined by only one intermolecular interaction that is significantly stronger than every other secondary interaction in the crystal lattice. Namely, N-H...N hydrogen bonded chains organize the crystal structures and only a few different arrangements of these chains are possible. However, these structures are flexible to some extent, and permit the alteration of the lattice parameters.

Most of the studied halogenated 2-phenylbenzimidazoles are isostructural. The exchange of the different halogen substituents causes slight changes in the crystal packing that on the whole results in a significant change in the lattice parameters. In the case of the different halogen substituents, the angle between the neighboring benzimidazole moieties varies from 60° to 130° . The length of the unit cell axes correlates with this angle and a nearly twofold increase can be observed in the length of the *c* axis in the series of iso-structural crystals. Financial support of the National Research, Development and Innovation Office (NKFIH) through OTKA K124544 is gratefully acknowledged.

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Keywords: supramolecular interaction, crystal engineering, benzimidazole

Altering the solid-state photochromic behavior of N-salicylideneanilines molecular switches by co-crystallization

Andrea Carletta¹, Nikolay Tumanov¹, Tom Leyssens², Benoît Champagne¹, Johan Wouters¹

- Namur Institute of Structured Matter (NISM), University of Namur, 61 rue de Bruxelles, Namur, Belgium
- Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain, Louvain-La-Neuve, Belgium

email: andrea.carletta@unamur.be

N-salicylideneaniline derivatives are among the most studied man-made thermo- and photo-switchable systems. These systems can switch between three different colored forms: an enol colorless form, a yellow cis-keto form and a red trans-keto form. A thermal tautomeric equilibrium between the enol and cis-keto form accounts for their thermochromism, whereas a cis-trans photoisomerization between the cis-keto form and the trans-keto form is the mechanism behind their photochromism. Photochromism can lead to a broad range of applications, i.e. in information storage and electronic display systems or in optical switching devices like ophthalmic glasses. However, due to the volume requirements of the cis-trans photoisomerization, photochromism is not easily encountered in the solid state. For this reason, we have used co-crystallization with the aim to induce photochromism in a non-photochromic N-salicylideneaniline chromophore. Our results (single-crystal structures and UV-vis diffusion reflectance) reveal how co-crystallization can be successfully employed for this purpose due to the fact that it changes both the free available volume of each molecule in the crystal and the intermolecular interactions.[1,2]

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Keywords: Co-crystals, photochromism, N-salicylideneanilines

MS32-P12

X-Ray study of new titanium (III) complexes derived from salicylic acid derivatives and N,N-bidentate ligands or monodentate O, N,-ligands

Peter herich1, Jozef Kožíšek1

 Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-81237, Bratislava, Slovakia

email: peter.herich@stuba.sk

The Titanium complexes stand for a new category of potential anticancer compound. The first studies of titanium complexes copied square-planar arrangement of cis-platin complexes. These complexes show a significant anticancer activity for a wide range of cell lines of cancer [1]. We synthesized new titanium complexes derived from salicylic acid derivatives (as 3-methoxysalicylic acid) and N,N-bidentate ligands (as 1,10-phenanthroline) or monodentate O, N,-ligands (as imidazole) [2]. These complexes were prepared in monocrystal form and suitable crystals were selected for X-ray experiment. All experiments were performed by Stoe STADIVARI diffractometer with a Dectris Pilatus 300 K detector and with an Genix3D Cu HF source (Cu-K α , λ = 1.54186 Å) at 100 K using a nitrogen gas open-flow cooler Cobra Oxford Cryosystems. Data reduction was performed using X-Area (Stoe, 2017) software package [3]. The crystal structures for measured compounds were solved in OLEX2 software using SHELXT-2015 program via Intrinsic Phasing and refined with SHELXL-2014 by least-squares procedure on F2. Since few efforts have been made towards the synthesis and use of titanium complexes as chemotherapeutic agents, this is an important area of our research.

Acknowledgement

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Keywords: anticancer activity, titanium complex, salicylic acid.
Playing hopscotch with pyridine@p-tertbutylcalix[6]arene crystal structures

Maura Malinska¹

1. Faculty of Chemistry, University of Warsaw, Warsaw, Poland

email: mmalinska@chem.uw.edu.pl

Calix[n]arenes have applications in the areas of host-guest chemistry, ion and molecular recognition, enzyme mimics, catalysis, interaction with biomolecules, ion extraction, and selective ion transport.[1] However, crystallisation of these systems is still challenging owing to their conformational flexibility. Therefore, crystallisation conditions (supersaturation, temperature, additives) were screened to obtain crystal structures with varying architecture such as channels and spherical voids with different conformations of the host. The molecular recognition and self-assembly between host p-tert-butylcalix[6]arene and guest pyridine led to kinetic trapping and crystallisation of the intermediate complexes, which were characterised by X-ray diffraction. The crystalline kinetic complex underwent slow spontaneous dissolution and subsequently recrystallises as thermodynamic inclusion complexes. Single-crystal X-ray diffraction revealed these first formed crystals to be the 15:1, 6:1 association complexes. These two crystal structures can transform into four different crystal structures depending on crystallisation conditions, forming 1:1, 1:1, 3:1, and 6:1 pyridine and p-tert-butylcalix[6]arene complexes. The crystal structure of the host-guest system can be tuned by the supersaturation changes and hydrogen-bonding properties of used additives to form crystal structures with designed architecture.

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Keywords: host-guest, crystallisation, complexes

MS32-P14

Self-assembly and gelation capability of *N*-Boc-protected tyrosine-based retropeptides

Mario Cetina1, Josipa Matić2, Debdeep Maity 2, Zoran Džolić2

- Department of Applied Chemistry, Faculty of Textile Technology, University of Zagreb, Zagreb, Croatia
- Division of Organic Chemistry and Biochemistry, Ruder Bošković Institute, Zagreb, Croatia

email: mario.cetina@ttf.hr

Gelators are compounds capable of solidifying various solvents and water. It has been shown that gel fibres are formed by the predominantly unidirectional self-assembly of gelator molecules through different types of intermolecular interactions. When the aggregates are sufficiently long, they entangle into a three-dimensional network capable of immobilizing the solvent. Considerable attention in supramolecular chemistry and materials science have received low molecular weight gelators (LMWGs). Potential for chemical variation among LMWGs is practically unlimited. The use of co-gelators, additives or solvent mixtures allows adjustment of the physical properties of gels for a range of applications, including template synthesis of nanoparticles and nanostructures, catalysis, drug delivery etc. One of the property of LMWGs is increasing possibility that a fully supramolecular approach can be achieved. Particularly attractive systems are those that can act as logic gates, with switchable behaviour that varies depending on the combination of thermal, optical and mechanical inputs [1-3].

Herein we present our recent investigation on gelation properties of oxalamide derivatives of tyrosine with tert-butyloxycarbonyl protecting group, by means of single-crystal X-ray analysis, scanning electron microscopy, transmission electron microscopy and atomic force microscopy. These derivatives differ in the length of the aliphatic chain (containing 2, 3, 5 or 6 methylene units) between tert-butyloxycarbonyl and oxalamide groups. Gelation property in these compounds is governed by strong intermolecular N-H···O hydrogen bonds between oxalamide groups and amide groups of the neighbouring molecules which form one-dimensional chain (see Figure). Such self-assembly appears to be one of the prerequisites for gelation behaviour of the compounds. Disposition of chains leads to the formation of channels with molecules of the crystallization solvent trapped within them.

Acknowledgement: This work has been fully supported by Croatian Science Foundation under the project IP-2016-06-5983.



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Keywords: self-assembly, gelators, oxalamides

MS32-P15

Supramolecular analysis of intramolecular H-bonds in (P,N) chelates and (P,C) palladacycles: towards understanding the mechanism of asymmetric induction *via* crystal engineering

Attila Benyei1, Gergely Farkas2, József Bakos2

- 1. Department of Physical Chemistry, University of Debrecen, 1 Egyetem tér., Debrecen, Hungary
- 2. Department of Organic Chemistry, University of Pannonia, 10 Egyetem u., Veszprém, Hungary

email: benyei.attila@science.unideb.hu

(P,N) chelates and (P,C) palladacycles [1] are very important complexes, especially in catalytic research. A set of pentane-2,4-diyl based chiral aminoalkylphosphine ligands Ph PCH(CH)CH CH(CH)NHR and their palladium complexes were prepared (as an example, see Figure). Single crystal X-ray diffraction; solution phase 1D and 2D NMR studies and theoretical calculations [2] were applied to verify the results and outcome of crystal engineering and to support catalytic studies. According to our latest results, mild oxidation of the complexes bearing suitable R substituents resulted in intramolecular C-H activation and concomitant formation of (P,C) coordinated palladacycles. Intramolecular H-bond between the coordinated chloride as acceptor and methylene/NH proton seems to play crucial role in stabilizing the conformation of the ring and fixing the stereogenic nitrogen atom, hence in transmission of chiral information in enantioselective catalysis. This opens the possibility to engineer suitable structures for enantioselective catalytic reactions of various substrates. Palladium was replaced with other metals having square planar coordination geometry and their structures were also studied.

Acknowledgement

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Keywords: supramolecular chemistry, hydrogen bond, enantioselective catalysis

Guest loading into highly flexible MOF pores driven by molecular recognition: a stepwise SCXRD investigation

Claudia Carraro¹, Davide Balestri¹, Paolo Pio Mazzeo², Paolo Pelagatti¹, Nicola Demitri³, Alessia Bacchi²

- 1. University of Parma, Parma, Italy
- University of Parma, Centro Interdipartimentale Biopharmanet-TEC, Parma, Italy
- 3. Sincrotrone Elettra, Trieste, Italy

email: claudia.carraro@studenti.unipr.it

MOFs (Metal Organic Frameworks) are a large class of ultraporous crystalline polymers deriving from the self-assembly of metallic ions or clusters with polytopic organic ligands. The high modularity of their synthesis allows a fine tuning of their porosity, making possible the confinement of molecular species of different shape and size.

Starting from the pioneeristic concept of crystalline-sponge method [1], we here propose a systematic way to embed small molecular aggregates inside home-made porous crystalline materials, with the aim of exploring the structural aspects of nanoconfinement and stabilizing the guest molecules inside the cavities of the structure. The challenge of this idea stands in the possibility to neatly "freeze", within a crystal, ordered supramolecular clusters of molecules that would form a liquid in their natural state at ambient conditions, and visualize their supramolecular aggregation, at different loading time.

In particular, we propose an unprecedent stepwise characterization of the evolution of the guest loading into metal-organic framework driven by host-guest interactions, focusing on the description of supramolecular aggregate of the guests inside the pores guided by guest-guest interactions. The MOF crystals were soaked for different time into the pure liquid guest and sequentially characterized via SCXRD.

The guest we focused on is eugenol, which is a volatile phenolic constituent of clove essential oil obtained from Eugenia caryophyllata buds and leaves. It is a functional ingredient of numerous products which have been used in the pharmaceutical, agro-food and cosmetic industry. The wide range of eugenol activities derived from it antimicrobial, anti-inflammatory, analgesic and antioxidant properties.

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Keywords: MOF, molecular recognition

MS32-P17

Synthetic strategies for delivering targeted supramolecular topologies of crystalline metal-containing solids

Marijana Đaković¹, Ivan Kodrin¹, Christer B. Aakeröy², Mladen Borovina

- 1. Department of Chemistry, Faculty of Science, University of Zagreb, Zagreb, Croatia
- Department of Chemistry, Kansas State University, Manhattan, United States of America

email: mdjakovic@chem.pmf.hrP

ractical crystal engineering, as a bottom-up approach for building-up functional materials, is transitioning from fundamental explorations to more targeted applications. This is illustrated by the fact that numerous productive strategies for non-covalent synthesis of organic solids-state systems have been reported.[1] In contrast, reliable synthetic protocols for the assembly of metal-containing systems, especially those that employ a combination of coordinate-covalent and relatively weak and readily reversible hydrogen and/or halogen bonds, have not received anywhere near the same attention.

To develop robust synthetic protocols for assembling metal-organic crystalline solids in a preconceived manner, we have focused our attention on several functionalities that are known to form robust and reliable supramolecular synthons in organic surrounding and examine their potential transferability to metal-organic systems. Coordination complexes often present additional challenges to the supramolecular chemist as they frequently contain functionalities and binding sites that can interfere with the intended crystal engineering strategy.

Here, we have carried out a systematic structural study of a number of classes of metal(II) complexes with pyridine-type and charge-balancing ligands, and rationalized their supramolecular behaviour against a back-drop of molecular electrostatic potential (MEP) surface values. Based on our extensive experimental data,[2-5] we are able to address several questions of critical importance to the successful assembly of metal-containing systems: (a) Under what conditions can we simply transfer specific synthons from organic to metal-organic solid-state systems? (b) Can a simplified electrostatic view of non-covalent interactions and the results from the calculated MEP values be used to direct and rationalize supramolecular synthesis? and (c) How can we derive supramolecular synthetic protocols in much the same way as classical synthesis is systematically altered and refined in response to product yields?

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Keywords: hydrogen bond, halogen bonds, supramolecular synthesis

Hydrogen bonding in organic salt hydrates

Laszlo Fabian1

1. School od Pharmacy, University of East Anglia, Norwich, United Kingdom

email: l.fabian@uea.ac.uk

About half of the drugs currently on market are salts. Salt based formulations are often preferred to those using neutral molecules, because they provide higher solubility. However, salts are prone to form hydrates, which may lead to stability problems with the drug product. The aim of this work is to investigate how specific hydrogen bonding interactions influence hydrate formation and whether the different propensities of ions towards hydrate formation [1] can be related to hydrogen bonding preferences.

The hydrogen bond coordination [2] of ammonium, chloride and carboxylate ions will be discussed using data from the Cambridge Structural Database [3]. Comparisons between hydrate and anhydrous structures of the same ion pair reveal how water-ion hydrogen bonding competes with direct anion-cation hydrogen bonds. For example, the average coordination number of ions is larger in hydrates, but the frequency of direct anion-cation bonds is reduced in hydrates relative to anhydrates. Similarly, the average number of ammonium ions bonding to a single anion is lower in hydrates than in anhydrous structures. Analysis of the hydrogen bonding environment of water in these structures shows clear differences between the anions and cations, e.g, in ammonium carboxylate salts water-carboxylate bonds are much more frequent than ammonium- water bond.

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Keywords: hydrogen bonding, hydrates, salts

MS32-P19

Magnetic properties of highly symmetrical compounds of cobalt(II) and nickel(II)

Marcin Koziel¹, Klaudia Nowakowska¹, Marlena Gryl¹, Dawid Pinkowicz¹, Wiesław Łasocha¹

1. Faculty of Chemistry, Jagiellonian University, Kraków, Poland

email: marcin.koziel@uj.edu.pl

The proper symmetry of crystal lattice determines the presence of many physical properties like piezo- or pyroelectricity, or nonlinear optical behaviour. [1] On the other hand the local symmetry of transition metal ions influences the energy of electron orbitals and, as a consequence, absorption of electromagnetic radiation as well as luminescent and magnetic properties. Therefore directing the synthesis towards particular symmetry of the solid product can allow control over the properties of resulting material. The aim of our current research includes the deeper understanding of the relation between the symmetry of the used building blocks and the symmetry of the products obtained in the self-assembly process. We also attempt to obtain products with high symmetry of the crystal lattice. It is quite a challenge for crystal engineering because highly symmetrical building blocks do not often yield highly symmetrical products. Such phenomena as partial dissociation, solvatation, intermolecular interactions or improper stoichiometry may render al efforts unsuccessful. Apart from inorganic compounds, where cubic system is quite common, in all other compounds the monoclinic and triclinic systems dominate. The most common orthorhombic group is adapted by c.a. 10% of structures, mostly chiral compounds, and the trigonal, tetragonal and hexagonal systems are the most rare.

In order to obtain the required features of the products we combined highly symmetrical organic molecules with various salts of 3d-elements. The inorganic component is introduced to improve stability of the compound as well as interesting electronic properties. We successfully obtained several new compounds, some of them belonging to high-symmetry space groups. The methodology, the structures and some interesting properties of the products will be presented.

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Keywords: symmetry, crystal engineering, magnetic properties

Molecular and crystal structure analysis of two new Oxazol-5-One derivatives

Merve İzmirli¹, İbrahim Hanif Nazlı¹, Derya Topkaya Taşkıran², Serap Alp², Muhittin Aygün³

- Graduate School of Natural and Applied Science, Dokuz Eylül University, İzmir, Turkey
- 2. Chemistry, Dokuz Eylül University, İzmir, Turkey
- 3. Physics, Dokuz Eylül University, İzmir, Turkey

email: izmirlimerve@yahoo.com

Two new oxazole-5-one derivatives, known as unsaturated azlactones, were synthesised due to the optical and biochemical importance [1,2]. These fluorescent molecules which are the cyclic anhydrides of N-acylaminoacids were formed by using Erlenmeyer azlactone reactions with aldehyde condensation. Molecular and crystal structures of 4-(N,N-diethylaminophenylmethylene)-2-(p-methoxyphenyl)oxazol-5-one (1) and 4-(N,N-diethylaminophenylmethvlene)-2-(p-nitrophenyl)oxazol-5-one (2) have been determined by single crystal X-ray diffraction method. The data collections were carried out with Rigaku Oxford XCalibur diffractometer, cell refinements and data reductions were executed using CrysAlisPro program [3]. Using Olex2, structures were solved with the SHELXT structure solution program and refined by full-matrix least-squares against F2 using SHELXL refinement package. The crystal structure of the compound 1 is stabilized $\pi - \pi$, C – H... π and C – H...O type weak interactions, while the crystal structure of the compound 2 is stabilized intermolecular $\pi - \pi$, N – $O_{\dots}\pi$ and $C - H_{\dots}O$ type weak interactions. There are also intramolecular C - H...N type weak interactions for both molecules.



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Corporation, Oxford, UK, 2015.

Keywords: azlactone, X-ray crystallography, weak interactions

MS32-P21

Molecules for electronics: Understanding their intramolecular properties towards their incorporation in devices

Berta Gómez-Lor¹, Angela Benito¹, Constanza Ruiz¹, Marcelo Echeverri¹

1. New Architectures in Materials Science, ICMM, CSIC, Madrid, Spain

email: bgl@icmm.csic.es

In recent years, the field of organic electronics has suffered enormous progresses. In fact, this area has evolved in only a few years from basic research to the development of devices such as organic light emitting diodes (OLEDs), organic photovoltaics (OPVs) and organic field effect transistor (OFETs) which are already reaching the market. The soft character of organic materials allows their solution processing and renders them very attractive in the development of flexible, light weight and low cost devices.

At the molecular level, fundamental parameters towards the incorporation of molecular materials in (opto)electronic devices -such as , light emission or absorption, energy levels...- can be designed "a la carte" thanks to the deep knowledge that has been acquired in the last few years through numerous structure-properties studies. However, properties of molecular materials are governed not only by those of individual molecules but also by the way they are spatially ordered. Single crystal analysis provides invaluable information on how molecules are arranged with respect to their surroundings and on the nature of intermolecular interactions among neighboring units in the bulk materials.

In this context we present here different examples of organic materials with light emitting and/or charge transport properties recently developed in our research group and show how a good understanding their intramolecular interactions (achieved through single crystal X-ray analysis) has allowed us to optimize their final properties.

Keywords: organic materials, charge transport, light emission

Structural determination of biological active N-phenyl-2phthalimidoethanesulfonamide derivatives

Muhittin Aygün¹, Resul Sevinçek¹, Duygu Barut Celepci¹, Özlem Akgül²

1. Physics, Dokuz Eylül University, İzmir, Turkey

2. Pharmaceutical Chemistry, Ege University, İzmir, Turkey

email: muhittin.aygun@deu.edu.tr

This study contains the structural characterization of un-N-phenyl-2-phthalimidoethanesulfonamide, substituted C₁₆H₁₄N₂O₄S, (I), the N-(4- nitrophenyl)-, C₁₆H₁₃N₃O6₈, (II), N-(4-methoxyphenyl)-, C16H16N3O6S, (III), and N-(2-ethylphenyl)-, as the monohydrate, C18H18N2O4S·H2O, (IV), derivatives in order to determine the impact of different substituents and their positions on intermolecular interactions and ultimately on the crystal packing. Studies of the effects of substituents on aromatic systems are of critical importance in chemistry, biology and pharmaceutics. The *n*-electron delocalization brought about by the substituent affects the intermolecular interactions and the packing motifs of aromatic molecules in crystals. Changes in the positions of substituent groups can significantly alter the molecular configurations and crystal structures of isomers. A slight difference in molecular structure can lead to a profound impact on the crystal packing. X-ray structural studies were performed with Rigaku-Oxford Xcalibur diffractometer. Data collections and reductions along with absorption corrections were performed using CrysAlis^{Pro} software package [1]. Structure solutions and refinements were performed using SHELXT and SHELXL, respectively, embedded in the Olex2 [2-4].



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Keywords: crystal structure, substituent position effect, ethanesulfonamide

MS32-P23

Four 2-Hydroxyethyl substituted NHC iodide complexes: structural characterization and theoretical comparisons

Duygu Barut Celepci¹, Aydın Aktaş², Yetkin Gök², Muhittin Aygün¹

1. Physics, Dokuz Eylül University, İzmir, Turkey

2. Chemistry, İnönü University, Malatya, Turkey

email: duygu.barut@deu.edu.tr

This study contains the structural characterization of four 2-Hydroxyethyl substituted N-heterocyclic carbene (NHC) iodide derivatives. Heterocyclic compounds are very important both industrially and biologically. These compounds are found in the vast majority of new drugs synthesized in the pharmaceutical industry. They are also used as ligands for the synthesis metal-N-heterocyclic carbene (NHC) complexes. In here, we report the molecular and crystal characterization of the NHC precursors. X-ray structural studies were performed with Rigaku-Oxford Xcalibur diffractometer. Data collections and reductions along with absorption corrections were performed using CrysAlis^{Pro} software package [1]. Structure solutions and refinements were performed using SHELXT and SHELXL, respectively, embedded in the Olex2 [2-4]. In the crystal structures, molecules are bonded to iodide anions through the O-H...I hydrogen bonds. Additionally, there are weak C-H...O interactions, which contribute to the stability of the crystal structures. One of the molecules is unsubstituted, and the others have methyl-substituents at the -ortho, -meta and -para positions on the benzene rings. We will also present the optimized geometries and the comparison of the frontier molecular orbital energy levels.



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Keywords: N-heterocyclic carbenes, iodide, crystal structure, DFT

MS33- Prediction of molecular crystal structures

Chairs: Dr. Jacco van de Streek, Dr. Aurora Cruz-Cabeza

MS33-P01

New potentials for accurate and efficient *ab initio* crystal structure prediction methods

David Bowskill¹, Isaac Sugden¹, Christina-Anna Gatsiou¹, Claire S. Adjiman¹, Constantinos C. Pantelides¹

1. Department of Chemical Engineering, Imperial College London, London, United Kingdom

email: david.bowskill13@imperial.ac.uk

Many organic molecules of industrial interest exhibit crystalline polymorphism, forming multiple solid-state structures, each potentially displaying different physico-chemical properties. This makes the discovery of new polymorphs both desirable from an R&D perspective and potentially disastrous from an operational standpoint. Consequently, understanding the crystal energy landscape of a commercial drug or chemical can be of great importance, especially if the compound is delivered in solid form, as is the case with suspended agrochemicals or oral pharmaceuticals. Current methods for crystal structure prediction (CSP) can be applied to molecules with limited conformational flexibility, although energy rankings are sometimes inaccurate. Furthermore, these methods become prohibitively expensive when the number of conformational degrees of freedom increases beyond 5 to 7.

We present recent progress on improving the accuracy and efficiency of a CSP method through changes to the interaction potential used, which enables the investigation of larger more flexible compounds. Our CSP method is based on the CrystalPredictor^[1] and CrystalOptimiser^[2] algorithms that a) efficiently explore the crystal energy landscape and b) accurately model leading contributions to lattice energy for predictions of stability and physical properties. We present a recently developed parameter estimation scheme for tailoring repulsive/dispersive contributions to the interaction potentials to crystal structure calculations, which leads to notable improvements in sublimation energy and structure reproduction with comparison to standard parameter sets.

We also introduce the concept of smoothed intramolecular potentials in CrystalPredictor, which offer near quantum-mechanical accuracy at much reduced computational cost. Such potentials make it possible to compute energy landscapes of increasingly large and conformationally flexible molecules through improved efficiency in the initial global search stage as well as increased accuracy in the resulting energy landscape. This, in turn, leads to a reduction in the number of structures that need to be further refined and hence further computational savings.

The above methods are demonstrated via application to both rigid and flexible molecules of industrial relevance.

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Keywords: Crystal Structure Prediction, Molecular Modelling, Computational

MS33-P02

Applying fast, accurate lattice energies for molecular crystal structure prediction using CrystalExplorer model energies

Peter Spackman 1, Graeme Day1

 School of Chemistry, University of Southampton, Southampton, United Kingdom

email: p.r.spackman@soton.ac.uk

The interaction energy between two molecules can be understood as a sum of several discrete terms [1]: generally electrostatic, polarisation (or induction), dispersion and exchange-repulsion ($E_{tot} = E_{elc} + E_{pol} + E_{dis} + E_{rep}$). Crystal-Explorer (CE) model energies [2], calibrated for use in intermolecular interactions, have been shown to estimate experimental crystal lattice energies [4] showing a favourable mean absolute deviation of only 6.6 kJ/mol from reference values in 110 crystal structures (the X23, G60, K7 and Z20 benchmark sets).

The relative energies of sets of crystal structures composed of the same molecular building blocks are of particular importance in crystal structure prediction (CSP), as lattice energy ranking is used as a primary predictor for the likelihood of a predicted structure being realized in the laboratory.

We investigate the potential use of CE lattice energies (and variations thereof) in CSP protocols – both in terms of relative energy ordering for different polymorphs and in terms of absolute energies – with reference to density functional and force-field based methods. Using CE lattice energies on the landscape of predicted crystal structures may constitute an accurate technique to improve predicted results, without the associated computational cost (and scaling) of periodic density functional calculations.

Keywords: Lattice Energies, CrystalExplorer, Polymorphism

MS34- Exploring structural dynamics in crystals

Chairs: Dr. Pance Naumov, Prof. Leonard Barbour

MS34-P01

Synthesis, characterization and photochemical properties of a series of new Ni and Cu nitro complexes chelated by the (N,N,O)-type ligands

Sylwia Kutyła¹, Radosław Kamiński¹, Adam Krówczyński¹, Dominik Schaniel², Katarzyna N. Jarzembskaa¹

- 1. Department of Chemistry, University of Warsaw, Żwirki i Wigury 101, 02-089 Warsaw, Poland, Warsaw, Poland
- CRM2, UMR 7036, Universite' de Lorraine, 54506 Vandoeuvreles-Nancy, France, Vandoeuvre-les-Nancy, France

email: sekutyla@gmail.com

Stimuli-responsive chemical systems in the solid state exhibiting specific photoactive properties have gained a lot of attention nowadays due to their potential technological applications (solar cells, LEDs, data storage assemblies, biological markers, etc.). It is, thus, of great importance to understand the phenomena behind the properties of interest, so as to design the desired materials and sensibly control their properties.

Hence here we present a detailed study of the photo-induced solid state linkage isomerism in a series of new Ni/Cu nitro complexes using spectroscopic methods (i.e., UV-vis, IR) physicochemical analyses (e.g., DSC), and advanced crystallographic approaches. The choice of these metals and substrates was dictated by their low price and abundance, which is in contrast to expensive literature-reported Rh or Pd complexes. [1,2] The desired photoswitchable materials should also be characterised by full conversions (100%), controllable reversibility, stability and preferably switching observable at temperatures closest to room temperature.

Our Ni complexes exhibit full conversion from the nitro to nitrito form when irradiated with the 590 nm or 660 nm LED light at 160 K, whereas the metastable state can be stable up to 240 K. To date, solely the Pd complex reported by Hatcher et al. [3] exhibited similar properties. In turn, the copper systems work best at 10 K, whereas the metastable form is usually stable up to 60 K, which makes them more difficult to be analysed and less applicable materials. It should be emphasized that the newly designed complexes can be relatively easily obtained and modified, and are fully air-stable.

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Figure 1.a) Molecular structure of the Ni^{II}–NO₂ complex based on the (N,N,O) chelating ligand at 100 K, b) Comparison of IR spectra for the ground and metastable state population at 10 K, for 590 nm LED.





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Keywords: nitro-complexes, photoswitches, photoisomers

MS34-P02

An isosymmetric supercritical-like transition in an organic semiconductor

Arie van der Lee¹, Gilles Roche², Guillaume Wantz³, Joël Moreau², Olivier Dautel², Jean-Sébastien Filhol²

- 1. Université de Montpellier, Montpellier, France
- Institut Charles Gerhardt de Montpellier, Laboratoire AM2N, UMR-5253, Université de Montpellier, ENSCM, CNRS, Montpellier, France
- 3. Université de Bordeaux, IMS, CNRS, Bordeaux, France

email: arie.van-der-lee@umontpellier.fr

We show that a high mobility thiophene-based organic semiconductor, BHH-BTBT, has an exceptionally large negative non-linear thermal expansion (-216 < α_2 < -333 MK⁻¹) between 95 and 295K along the crystallographic b-axis, being compensated by an even larger positive expansion in the perpendicular direction (287 < α_1 < 634 MK⁻¹) [1]. The temperature evolution of the angle between neighbouring thiophene moieties and the optical band gap show a clear transition around 210 K but no space group change is detected, *i.e.* the transition is isosymmetric. A complete theoretical characterization of BHH-BTBT using ab initio molecular dynamics shows that below ~ 200 K two different domains exist of which one is dominant but which dynamically coexist around and above 210 K. This transition is reminiscent to the 'diffuse' or 'crossover' phase transition analyzed theoretically by Christy [2] that leads to solid-state supercritical behaviour. The origin of the extreme negative and positive thermal expansion is related to a steric hindrance between adjacent tilted thiophene units and strongly enhanced by attractive S…S and S…C interactions within the highly anharmonic dynamic mixed-domain phase.

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Keywords: thermal expansion, phase transition, supercritical transition

MS34-P03

Pressure-induced metal-metal bond formation and HOMO-LUMO inversion in a single component Pt-based molecular crystal

Hamish Yeung¹, Chloe Coates¹, Andrew Goodwin¹, Hengbo Cui², Reizo Kato², Takao Tsumuraya³, Mark Warren⁴, David Allan⁴ Dominik Daisenberger⁴

- 1. Inorganic Chemistry Laboratory, University of Oxford, Oxford, United Kingdom
- 2. Condensed Molecular Materials Laboratory, Riken, Wako-shi, Japan
- Magnesium Research Center, Kumamoto University, Kumamoto, Japan
- Diamond Light Source Ltd, Harwell Science and Innovation Campus, Didcot, United Kingdom

email: hamish.yeung@chem.ox.ac.uk

The discovery of the first organic metal based on tetrathiafulvalene (TTF) in the 1970's resulted in an explosion of interest in the exotic electronic properties of molecular materials.[1] In these charge transfer salts, electronic properties are governed by the interactions between frontier molecular orbitals (HOMO and LUMO interactions), which control the band gap and charge carrier generation. Design of single-component molecular conductors is difficult, however, because the HOMO-based and LUMO-based bands tend to be well-separated from each other, leading to insulating behaviour. We and others have found that application of pressure can be a useful tool with which to alter the HO-MO-LUMO overlap and broadening of the bands, resulting in metallic[2] or even superconducting behaviour.[3]

We report a combined experimental and computational study of the single component molecular crystal [Pt(dddt),] (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate), which undergoes a remarkable first-order single-crystal to single-crystal transition under pressure. X-ray diffraction measurements show that the ambient pressure offset-dimer structure converts to a face-to-face dimer above 5 GPa, accompanied by a dramatic reversal in the lengths of the crystal *b*- and *c*-axes. First principal electronic structure calculations show that the change in dimer geometry causes an inversion of the energies of the HOMO and LUMO bands. This enables the formation of a rare unsupported Pt-Pt bond that drives the transition and gives rise to metallic conductivity at pressures above 10 GPa.

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Keywords: High pressure, Molecular metal, Phase transition

MS35- From 0- to 3-dimensional porous systems

Chairs: Dr. Felipe Gandara, Prof. Wendy Queen

MS35-P01

Negative compressibility of a metal-organic framework?

Szymon Sobczak1, Andrzej Katrusiak1

1. Department of Materials Chemistry, Adam Mickiewicz University, Poznań, Poland

email: szymon.sobczak@amu.edu.pl

Fundamental thermodynamics requires that all materials reduce their volume at high pressure. Owing to specific anisotropic features, originating from various structural motifs, some compounds can elongate in one or two directions, which is termed as negative linear and area compressibility.1 The volume compression restriction applies to constant composition materials (i.e. closed systems). It was evidenced that zeolites and other porous materials can uptake the guest molecules from gaseous and liquid surrounding, which can increase the crystal volume despite the increasing pressure.² These are so called open systems. In those high-pressure experiments, various simple molecular fluids (water, methanol, ethanol, etc.) and their mixtures were used. The transport of guest molecules can be eliminated by compressing the sample in liquids composed of molecules much larger than the dimensions of pores, for example in oils.

We have performed a series of such experiments for a newly synthesized 2D metal-organic framework Ni(hip) (bipy)(H₂O)₂ · H₂O · CH₃OH · DMF, denoted as AMU-2 (where AMU abbreviates Adam Mickiewicz University). Its flexible structure is built of 4,4'-bipyridines (bipy) and 5-hydroxyisophthalic acid anions (hip) into grids further connected by H-bonds. The compression of AMU-2 revealed its unpreceded elastic and sorption-elastic properties. Hydrostatic compression performed in three different large-molecule liquids (oils Daphne 7373 and NVH or Fluorinert FC-77) result in a significant volume expansion of about 120 Å3 at 0.2 GPa. This counterintuitive effect mimicking the negative volume compression was observed by X-ray diffraction for several samples. We have shown that this porous material, when compressed in oils, partially collapses and becomes amorphous, which triggers a transport of guest molecules present in the pores to the crystalline parts of the sample. This mechanism of transport of gests induced be external stimulus of pressure has been described as a 'zone-collapse' effect.3



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Keywords: metal-organic framework, high-pressure, volume compression, amorphization

MS35-P02

A novel bismuth-containing metal-organic framework: the first example of a flexible bismuth MOF

- Erik Svensson Grape¹, Hongyi Xu¹, Ocean Cheung², A. Ken Inge¹
- Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden
- Division for Nanotechnology and Functional Materials, Department of Engineering Sciences, The Ångström Laboratory, Uppsala University, Uppsala, Sweden

email: erik.grape@mmk.su.se

Despite the large number of published metal-organic frameworks (MOFs), only a handful of microporous structures which contain bismuth have been published so far [1, 2]. Unlike coordination polymers synthesized from other metal cations, bismuth cations have rather high coordination numbers and unusual coordination geometries, leading to highly unpredictable and unique structures. Additionally, bismuth is interesting for potential pharmaceutical applications as it has been shown to be biologically active and potentially a future aid in relieving problems with multi-resistant bacterial strains [3].

In order to achieve a better understanding of the chemistry of bismuth in inorganic-organic hybrid structures, four new bismuth-containing structures have been synthesized. The reagents used where bismuth and a tritopic organic linker. One of the acquired phases proved to be a porous metal-organic framework, which undergoes reversible structural changes upon activation of the framework, thus being the first example of a flexible bismuth MOF. The structures were solved using single crystal X-ray diffraction (SCX-RD), X-ray powder diffraction (XRPD) and continuous rotation electron diffraction (ED). Continuous rotation ED may greatly aid in the characterization of microcrystalline materials, which are often acquired when synthesizing bismuth-containing compounds. The structural changes occurring have been inferred from Rietveld refinement against XRPD data and will be discussed extensively.

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Keywords: metal-organic frameworks, Rietveld refinement, hydrothermal synthesis

Solvomorphism in the active pharmaceutical ingredient bismuth subgallate: microporous 1D, 2D and 3D coordination polymers

Ken Inge¹, Victoria Rooth¹, Erik Svensson Grape¹, Sofia Takki¹, Tom Willhammar¹

 Department of Material and Environmental Chemistry, Stockholm University, Stockholm, Sweden

email: andrew.inge@mmk.su.se

Bismuth is heaviest nonradioactive metal, yet its compounds generally have very low toxicity and have been used as active pharmaceutical ingredients (APIs) for nearly three centuries. Bismuth subgallate, a compound comprising of Bi³⁺ cations and the organic ligand gallic acid, has been used in medical applications since at least the 1890s for its antimicrobial, hemostatic, astringent, and deodorizing properties. The material has been used in wound therapy and the treatment of gastrointestinal disorders, and is still used as the API in several over-the-counter drugs today. Yet, despite its century-long use in medical applications, the crystal structure of bismuth subgallate long remained elusive due to complications that arise from its small crystal size.

We recently determined the crystal structure of bismuth subgallate, using continuous rotation electron diffraction. The technique, which is performed in a transmission electron microscope (TEM), allows for the fast acquisition of 3D diffraction data on crystals with diameters on the nanometer length scale.[1] The very fast data acquisition of 3D data, which takes 1-3 minutes in total, is essential for minimizing beam damage to the crystals. Structure determination of bismuth subgallate revealed that the material is a microporous 1D coordination polymer.[2] Knowledge of the structure led to the discovery of new properties of the materials. Gas sorption experiments indicated a high selectivity for CO2/ N2 gas separation; the crystal structure was observed to be rather robust for a coordination polymer and remains intact even after stirring the material in HCl solution (pH = 2) and phosphate buffered saline solution for at least several hours. Two novel solvomorphs of bismuth gallate were also synthesized and their structures were also solved by continuous rotation electron diffraction. One is a 3D framework structure consisting of bismuth-oxo rods, while the other consists of the same rods but condensed into layers resulting in a 2D layered crystal structure.

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Keywords: bismuth, coordination polymers, active pharmaceutical ingredient

MS35-P04

Design of new bi- and tri-periodic indium MOFs and their catalytic activity in the Strecker and Ugi multicomponents reactions

Daniel Reinares Fisac¹, Lina María Aguirre-Díaz¹, Marta Iglesias¹, Enrique Gutiérrez-Puebla¹, Felipe Gándara¹, M. Ángeles Monge¹

 Materials Science Factory, Department of New Architectures in Materials Chemistry - Materials Science Institute of Madrid (ICMM), Spanish National Research Council (CSIC)., Madrid, Spain

email: daniel.reinares@icmm.csic.es

Metal-organic Frameworks (MOFs) are a type of materials made of the combination of organic linkers and metal centres. [1] Our group has extensively carried out research focused on the design and preparation of MOFs with group 13-elements, which have shown great potential in the field of heterogeneous catalysis. [2] In particular, indium-MOFs have shown remarkable activity as Lewis-acid catalysts for multicomponent reactions (MCRs) such as Strecker and Ugi reactions (involving the reaction of ketones, amines and cyanides in the former, and aldehydes, amines, carboxylic acids and cyanides in the later). With the use of In-MOFs, these MCRs can be carried out in one step and under Green conditions by reducing the amount of solvent, at room temperature, and reaching high yields. We have prepared three different MOFs with the combination of indium and the tritopic linker 1,3,5-Tris(4-carboxyphenyl)benzene (H₃btb), denoted InPF-110, InPF-50, and InPF-51. InPF-110 exhibits a mesoporous, three-periodic structure formed by trimetric inorganic secondary building unit with the metal centres in octahedral coordination environment. This MOF, which allows the diffusion of multiple substrate inside the pores, has demonstrated exceptional activity in the Strecker reaction. On the other hand, InPF-50 and InPF-51 exhibit two periodic structures with entangled layers. Presence of metal centers with low coordination number, large number ofaccessible open-metal sites, and presence of Lewis basic centers result in excellent catalytic activity of these MOFs in the Ugi reaction.

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Keywords: MOF, catalysis, porous

Organometallosiloxanes and germoxanes as porous materials

Alexander Korlyukov¹, Anna Vologzhanina¹, Alexander Goloveshkin¹, Marina Es'kova¹, Alexei Bilyachenko¹

1. INEOS RAS, Moscow, Russia

email: akorlyukov@gmail.com

Metallosiloxane $M_nM'_m[RSiO_{1,5}]_n$ and metallogermoxane $M_nM'_m[RGeO_{1,5}]_n$ cluster units (M = transition metal, i.e. Cu, Co, Ni, Fe, M' – alkali metal, i.e. Na, K, Cs, Rb, n = 2-7, m = 2 - 10) are relatively rigid polynuclear nanosized units possessing catalytic [1] and magnetic [2] properties. The shape and size of cluster units generally governed by the nature of transition metal and synthetic conditions, while the nature of alkali metal and solvent affect connectivity of these cages [3]. Rigidity of cages is responsible for realization of supramolecular and coordination architectures with open channels and voids up to 15 Å. Moreover, as coordination polymers are formed by M-O and M'-O interactions only, these porous architectures remain stable up to 400°C when the organic coating is decomposed [3a].

In this study we discuss the effect of M, M' and E (E = Si, Ge) nature on the shape and connectivity of cluster units, the topology and abundance of 1D, 2D and 3D architectures based on organometallosiloxanes and germoxanes, and synthetic pathways to form porous 2D and 3D nets. Multitemperature PXRD data of various compounds are compared to investigate thermal stability of the title compounds and their ability to form purely inorganic molecular sieves. The latter can be used for catalysis and gas sorption.

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Keywords: metallosiloxanes and metallogermoxanes, networks, topology

MS35-P06

Pressure-induced solid-state reactions of coordination polymers

Aleksandra Półrolniczak1, Szymon Sobczak1

1. Department of Materials Chemistry; Adam Mickiewicz University, Poznań, Poland

email: aleksandra.polrolniczak@amu.edu.pl

Metal-organic frameworks (MOF's) and Coordination Polymers (CP's) are classified as the interdisciplinary field between the coordination and inorganic chemistry. For decades, these porous materials have been thoroughly investigated because of their potential applications, such catalysis and sensing as well as the storage of fuel gases and water.¹ Presently, high pressure has become an established highly-efficient tool for inducing strong structural transformations in various compounds.² In particular high pressure can be applied for post-synthetic modification (PSM) of CP's. Several approaches have been used for PSM, but the category of pressure induced modifications has merely begun to emerge.

Herein we present 2-dimensional cadmium coordination polymer Cd(APP)₂NO₃ · NO₃ [APP abbreviates 1,4-bis(3aminopropyl)piperazine], undergoing a pressure induced associative reaction to cis-Cd(APP)2(NO3)2. Our high-pressure structural measurements revealed that at 0.4 GPa a rearrangement of the Cd-coordination sphere takes place, which is connected with the formation of a new additional coordination bond. As a result of this reaction, a nitrate anion, detached of the cation and located in the crystal void space in the phase I, is transferred to the metal center. Consequently, the cadmium ligancy increases from 6 to 7 in phase II. The high-pressure reactivity of CP's can be explained by three simple rules: involving the metal/ligand ionic radii ratio, the elimination of potential voids in the compressed structure as well as the vicinity from the metal center to reacting anions.

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Keywords: Coordination Polymers; high pressure; new bond formation

Extended networks based on nickelsiloxane units

Marina Eskova1, Alexander Korlyukov1

1. INEOS RAS, 119991, GSP-1, Moscow, V-334, Vavilova St. 28, Russia, Moscow, Russia

email: marinaeskovskaya@gmail.com

New family of bi-, tetra-, penta-, and hexanickel cage-like phenylsilsesquioxanes 1-3 (Fig.1) was obtained by self-assembling and transmetalation procedures. Their crystal structures were established by single crystal X-ray analysis; and features of crystal packing relevant to the networks formation were studied by a topological analysis. The geometry of metallosiloxane units 1 and 2 could be assigned to a distorted prism, with prominent shift of prism' bases (silsesquioxane ligands) from the vertical axis. In turn, molecular architecture of compound 3 is regular prismatic one. Compounds 1-3 form extended networks in crystal via coordination bonds between alkali metals (Na, K, Cs) and oxygen atoms of siloxanolate moieties or coordinated solvent molecules (see, for instance Fig. 2). The investigation of magnetic properties revealed the presence of ferro- or antiferromagnetic interactions between Ni(II) ions giving rise in the most cases the presence of a slow relaxation of the magnetization, which can arise from the spin frustration.

sic Research (projects 16-29-05180 and 16-03-00206). Keywords: nickelsiloxanes, coordination polymers, magnetic properties, topology

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MS35-P08

Engeneering novel poruos 3D metallacrown-frameworks, through the ligand periphery design

Vittoria Marzaroli¹, Luciano Marchió², Giulia Spigolon³, Giulia Licini³ Vincent L. Pecoraro⁴, Matteo Tegoni²

- 1. University of Parma, Parma, Italy
- Department of Chemical Sciences, Life Sciences, and Environmental Sustainability, Università di Parma, Parma, Italy
- 3. Chemistry Department, University of Padova, Padova, Italy
- 4. Chemistry Department, University of Michigan, Ann Arbor, United States of America

email: vittoria.marzaroli@studenti.unipr.it

Metallacrowns are metallamacrocycles characterized by the (M-N-O)_nconnectivity and originated by self-assembly of bischelating ligands (e.g. hydroxamic acids) and metal ions. Properties and structure of this class of compounds are tunable through a wise choice of the building blocks set. [1] Moreover a relatively large amount of metal ions are confined in a small molecular volume, resulting in peculiar chemical physical features, such as luminescence or single-molecule magnets behavior. [2]

We present here three new metallacrowns-based materials, that were prepared using salicylhydroxamic acid derivatives as ligands and Mn(II/III) as metal ion.

The salicyhydroxamic acid (H₃Shi) react with Mn, forming a tightly packed, not porous coordination polymer. The nodes are endeca-manganese clusters, resembling a 3-blade propeller, where each blade is a half of a 16-metallacrown-6. Both the amino (H₃p-aShi) and the pyridyl (H₃p-pyShi) derivatives result in a novel porous arrays having the same Mn₁₁cluster node. The amino function of H₂p-aShi drives the propellers to interact through sodium ions and supramolecular interactions (i.e. hydrogen bonds). The resulting architecture shows hexagonal channels, which correspond to 39 % of the unit cell volume. The pyridyl function of H₃p-pyShi coordinates one Mn of the neighboring propeller. As a result H₂p-pyShi originates a metallacrown-based network, which shows channels in all the three dimensions and has cavities corresponding to 55% of the unit cell volume. The array, shown in the Figure, can be considered a novel metal-organic-framework with an endeca-Mn node.



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Keywords: metallacrown, metal-organic-frameworks, liganddesign

MS35-P09

X-ray study of metal-organic framework compounds

Marek Fronc¹, Jozef Kožíšek¹, Lucian G. Bahrin², Lilia Clima², Sergiu Shova², Vasile Lozan²

- Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-81237, Bratislava, Slovakia
- The "Petru Poni" Institute of Macromolecular Chemistry, no. 41A Grigore Ghica Voda Alley, 700487, Iasi, Romania

email: marek.fronc@stuba.sk

Metal-organic frameworks (MOFs) are porous materials consisting of inorganic metal nodes, known as secondary building units, bridged together by organic linkers. In the past few decades, MOFs have attracted a great deal of attention due to their potential applications in heterogenous catalysis, controlled drug release, selective adsorption or gas storage and separation. [1]

The organic ligand 3,3,5, 5'-Tetrakis(4-carboxyphenyl)bimesityl (H_4L) used by us in the synthesis of several new MOFs was obtained through a Suzuki coupling reaction [2] between 3,3',5,5'-tetraiodobismesitylene and 4-carboxyphenylboronic acid, in the presence of tetrakis(triphenylphosphine)palladium (0) as a catalyst. The MOFs were obtained by mixing the appropriate metals salt with H_4L in DMF (Zn, Cd) or DMF/water (Mg, Ca, Na) in solvothermal conditions(heating at 80 °C for 48-72 hours).

All diffraction experiments were performed at Stoe STAD-IVARI diffractometer with a Dectris Pilatus 300 K detector and with an Genix3D Cu HF source (Cu-K α , $\lambda = 1.54186$ Å). Data were collected at 100 K with the use of a nitrogen gas open-flow cooler Cobra Oxford Cryosystems. For data reduction X-Area (Stoe, 2017) software package [3] was used. The crystal structures were solved and refined in OLEX 2 software using SHELX suite of programs.

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Keywords: Metal-Organic Framework

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Exploring the catalytic performances of a series of bimetallic MIL-100(Fe-Ni) MOFs

Monica Gimenez-Marques¹, Andrea Santiago-Portillo², Sergio Navalón², Farid Nouar³, Hermenegildo Garcia², Christian Serre³

- Instituto de Ciencia Molecular (ICMol), Universidad de Valencia, c/ Catedrtico Jos Beltran, 2, 46980 Paterna, Spain, Paterna, Spain
- 2. Department of Chemistry and Instituto de Tecnologia Quimica (ITQ-CSIC-UPV)., Valencia, Spain
- Institut des Matériaux Poreux de Paris, Ecole Normale Supérieure, Ecole Supérieure de Physique et de Chimie Industrielles de Paris, FRE CNRS 2000, Paris Research University, 75005 Paris, France., Paris, France

email: monica.gimenez-marques@uv.es

The development of multifunctional solid catalysts is currently of foremost relevance in the field of heterogeneous catalysis. The reason is that it is expected that bi/multi-functionalization achieve specific reactions in one single step thus noticeably reducing processing costs. In this context, Metal-Organic Frameworks (MOFs) can play a crucial role given their chemically modulable nature and their already proved suitable performance as solid heterogeneous catalysts for specific liquid phase chemical transformations. The synthesis of stable mixed-metal MOFs however, is not always obvious and requires a control of the metal stoichiometry based on cations with different oxidation states and therefore very distinct chemical reactivities.

In this work we present a series of mixed-metal Fe^{III}/Ni^{II} MOFs of the MIL-100 type material containing different metal ratios. The resulting heterometallic MIL-100(FeNi) materials maintain thermal, chemical and structural stability with respect to the parent MIL-100(Fe) MOF as can be deduced from XRPD, N2 adsorption, FTIR and thermal analysis. The nature and the oxidation state of the accessible cations have been evaluated by in situ infrared spectroscopy analysis. The obtained mixed-metal MIL-100(FeNi) MOFs and the parent MIL-100(Fe) material have been evaluated as heterogeneous catalysts in a model acid-catalyzed reaction such is the Prins reaction. It is found that the catalytic activity improves more than one order of magnitude for a certain metal substitution, with a complete selectivity for the formation of Nopol. The proposed mechanism will be discussed.

Keywords: MOFs, heterogeneous catalysis

MS35-P11

Sulfur polyconjugated organic ligands as bulding block in photoactive metal-organic frameworks

Alba García Sánchez¹, Marta Liras¹, Fernando Fresno¹, Mariam Barawi¹, Enrique Gutiérrez-Puebla², Ángeles Monge², Felipe Gándara², Víctor A. de la Peña O'Shea¹

- 1. Photo Activated Processes Unit, IMDEA Energy, Móstoles, Spain
- 2. Instituto de Ciencia de Materiales de Madrid, CSIC, Madrid, Spain

email: alba.garcia@imdea.org

Metal-organic frameworks or MOFs, are relative recent hybrid structures form by the joint between metal clusters and organic ligands. These networks have raised notable research interest because of their components are responsible for the structure properties resulting in a wide range of applications. Therefore, the appropriate choice of these building blocks could improve its features and direct the properties towards different applications like catalysis, gas separation and storage, magnetism, sensors, drug delivery [1].

Here we report the synthesis of photoactive MOFs with the combination of hole transport sulfur-conjugated ligands and different metals such as bismuth and indium. The use of electroactive organic ligands can provide charge transfer phenomena in these tridimensional networks and can leads to significant electronic interactions with the metal center-coordinated metal ions under light irradiation leading to an improvement of the optoelectronic and photo-catalytic properties [2]. In addition, a metal-node with relative large ionic radius with possibility of act with high oxidation state and empty orbitals to accept electron transfer is desired.

The opto-electronic and conductive properties of these networks have been determined by several characterization tools. Transient absorption spectroscopy reveals different electron-hole recombination rates compared with the corresponding metal oxides. Moreover, photocurrent measurements reveals changes in the conductivity in function of the used metal node.

In this way we have study the expected potential properties of these specifically tailored structures to their application into photocatalytic reactions.



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Keywords: Metal-organic frameworks, conjugated ligands, charge transfer

MS35-P12

Structural flexibility in the solid state

Len Barbour¹

 Department of Chemistry and Polymer Science, University of Stellenbosch, Stellenbosch, South Africa

email: ljb@sun.ac.za

In order to understand solid-gas inclusion processes at the molecular level it is important to correlate physico-chemical data (e.g. sorption isotherms and calorimetric analysis) with structural data. It is therefore desirable to carry out structural elucidation and calorimetric analysis under conditions that closely mimic those of the sorption/desorption experiments. However, the crystallographic analysis of samples under controlled gas environments poses significant technical challenges, particularly given the limited space associated with the sample compartment of standard commercial diffractometer. In this regard, an environmental gas cell has been developed in parallel with a pressure-programmed differential scanning calorimeter. Use of these complementary techniques has provided new insight into features such as pressure-induced phase transformations that give rise to inflections and hysteresis in sorption isotherms. The influence of guest molecules on aspects such as structural flexibility and changes in network interpenetration will be discussed.

Keywords: porosity, structure-property relationships, in situ analysis

New uranyl compounds with microporous frameworks

Evgeny Nazarchuk¹, Oleg Siidra¹, Dmitry Charkin², Wulf Depmeier³

- Department of Crystallography, Saint-Petersburg State University, Saint-Petersburg, Russia
- 2. Department of Chemistry, Moscow State University, Moscow, Russia
- Institut f
 ür Geowissenschaften der Universit
 ät Kiel, Kiel, Germany

email: e_nazarchuk@mail.ru

The first microporous framework structures containing uranium and chromium have been synthesized and characterized. $Rb_2[(UO_2)_2(CrO_4)_3(H_2O)_2](H_2O)_3$ (1) was crystallized from uranyl chromate solution by evaporation. Further evaporation led to increased viscosity of the solution and overgrowing of Rb₂[(UO₂)₂(CrO₄)₃(H₂O)](H₂O) (2) on the crystals of 1. With respect to 1, the framework of 2 is partially dehydrated. Both frameworks differ compositionally by only one water molecule, but this seemingly small difference affects significantly the pore size and overall structural topology of the frameworks, which present very different flexibility of the U-O-Cr links. These are rigid in the pillared framework of 1, in contrast to 2 where the U-O-Cr angles range from 126.3 to 168.2°, reflecting the substantial flexibility of Cr-O-U connections which make them comparable to the corresponding Mo-O-U links in uranyl molybdates.

Α new organically templated uranyl sulfate. $(pyrH^+)_2[(UO_2)_6(SO_4)_7(H_2O)_2]$ (3) was obtained by slow evaporating from the solution containing uranyl nitrate, sulfuric acid and pyridine. The crystals of 3, within two weeks, in the mother liquor gradually disappeared, followed by the simultaneous crystallization of framework $(pyrH^+)(H_3O)[(UO_2)_3(SO_4)_4(H_2O)_2](H_2O)$ (4) and layered $(pyrH^+)_2[(UO_2)_2(SO_4)_3]$ (5). The frameworks, in the structures 3 and 4, contain channel systems with sizes 12.4×10.2 and 12.9×10.8 Å, respectively. Change of frameworks densities and structural complexity after the recrystallization is discussed

In the crystal structures of $Na_2(SO_3OH)(mfaH^+)[(UO_2)(SO_4)_2]$ (6) and $Na(mfaH^+)[(UO_2)_2(SeO_4)_3(H_2O)](H_2O)_2$ (7) uranyl-sulphate and uranyl-selenate units are interconnected via sodium complexes with mfa into metal-organic frameworks. Both frameworks contain the channels of 10.2×9.8 and 12.8×5.4 Å in 6 and 7, respectively.

Until recently, crystal structures of uranyl compounds containing inorganic nanotubes were known only for uranyl-selenate systems. There are three known topological types of nanotubes with internal diameters of ~7 Å and ~15 Å. Uranyl sulfate Na(phgH⁺), $[(UO_2)_6(SO_4)_{10}](H_2O)_{3.5}$ (1) was obtained at room temperature by evaporation from aqueous solution. Its structure contains unique uranyl sulfate $[(UO_2)_6(SO_4)_{10}]^8$ nanotubules templated by protonated N-phenylglycine ($C_6H_5NH_2CH_2COOH$)⁺. Their internal diameter is 14 Å.

A comparative crystal chemical analysis of new and previously described micro - and mesoporous framework uranyl compounds will be discussed. This work was financially supported by the Russian Science Foundation through the grant 16-17-10085. Technical support by the SPbSU X-ray Diffraction Resource Centre is gratefully acknowledged.

Keywords: micro - and mesoporous framework uranyl compounds, uranyl nanotubules

MS36- Structure and function in inorganic and coordination complexes

Chairs: Dr. Attila Benyei, Prof. Alessandra Crispini

MS36-P01

Luminescent π - π -assembled complexes of Zn and Cd with anthracene functionalized ligands

Serhii Vasylevskyi, Dario Bassani¹, Katharina Fromm²

- 1. Chemistry department, University of Bordeaux, Bordeaux, France
- Chemistry department, University Of Fribourg, Fribourg, Switzerland
- email: serggiy92@gmail.com

The most promising materials nowadays in the field of soft materials coordination compounds are the compounds able to produce and harvest great luminescent properties. In this respect coordination polymers with highly emissive light fluorophores are the most attractive. Introducing highly luminescent fluorophores into rigidifying net or framework could enhance the stability and versatility of the material in application in different fields of technologies such as sensors¹, non-linear optics², up-conversion materials³.

The main goal of this study is to investigate the luminescent properties of new coordination polymers of Zn(II) and Cd(II) with highly luminescent new anthracene fluorophores. The study of photoluminescent properties with quantifying the lifetime and quantum yield with respect to the crystal structure of Zn(II) and Cd(II) coordination polymers will be presented. The first part will include fundamental studies to understand structure integrity with optical properties observed. And the second will include the part of tight description of this correlation with a stepwise tunable approach to luminescence by inserting different guest interaction will be also described and studied.

Different coordination polymers with Zn(II) and Cd(II) will be presented, synthesized on the basis of 9-substituted anthracene building blocks (fig.1.), their luminescent properties will be discussed as well.



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Keywords: coordination polymers, luminescence, anthracene complexes.

Powder X-ray diffraction structural characterization and applications of cis-[Co^{II}(κ^2 N,N'-1,10-phenanthroline-5,6-dione)₂Cl₂

Olufunso Olumide Abosede1, José Fernandes2, Simona Galli2

- 1. Department of Chemistry, Federal University Otuoke, Otuoke via Yenagoa, Nigeria
- Dipartimento di Scienza e Alta Tecnologia, Università dell'Insubria, via Valleggio 11, 22100, Como, Italy

email: abosedeoo@fuotuoke.edu.ng

1,10-phenanthroline-5,6-dione (phendione) is a versatile ligand that has been used in the preparation of stable homoand hetero-metallic complexes with a wide range of transition metal ions [1]. Phendione itself possesses electrochemical and strong biological activity including antifungal, DNA and cytotoxic activity [2-3]. It has been shown that its biological activity increases upon complexation with a wide range of metal ions, such as Ag⁺, Cu²⁺, Pt²⁺ [2-3].

This poster presents the synthesis and powder X-ray diffraction (PXRD) structural characterization of cis-[Co^{II}($\kappa^{2}N$,N'-1,10-phenanthroline-5,6-dione)₂Cl₂]. PXRD details, unit cell parameters, and space group for cis-[Co^{II}($\kappa^{2}N$,N'-1,10-phenanthroline-5,6-dione)₂Cl₂], C₂₄H₁₂Cl₂CoN₄O₄, are reported [a = 41.4951 (13) Å, b = 8.2768 (2) Å, c = 12.4994 (3) Å, unit cell volume V = 4292.9 (2) Å³, Z = 8, and space group Fdd2].

Spectroscopic characterization and the antibacterial activity of this complex against Bacillus subtilis, Staphylococcus epidermidis, Staphylococcus aureus, and Klebsiella pneumonia will also be presented and discussed.



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Keywords: powder X-ray diffraction, 1,10-phenanthroline-5,6dione, crystal structure

MS36-P03

The dimeric nature of the Re(I) complexes of the thiosemicarbazonate derived of 4-(dimethylamino)benzaldehyde

Saray Argibay Otero1, Ezequiel Vázquez-López1, Rosa Carballo1

1. Departamento de Química Inorgánica, Instituto de Investigación Sanitaria Galicia Sur-Universidade de Vigo, Vigo, Spain

email: saargibay@uvigo.es

Dimeric thiosemicarbazonate complexes $[\text{Re}_2(\text{CO})_6(\text{L})_2]$ (see Figure 1) are often isolated from solutions of the corresponding mononuclear rhenium(I) complexes, $[\text{ReX}-(\text{CO})_3(\text{HL})]$, containing the protonated species of those bidentated ligands [1]. The deprotonation of the HL ligand and the labilization of the halogen in adduct produces the dimerization of the rhenium complexes by linking the sulfur atom of a neighboring molecule at the position previously occupied by the halogen atom. The Re–S bond to the sulfur atom belonging to the chelating system of the neighboring rhenium atom is larger (around 0.1 Å) than its own chelate.

When basic media is used to remove the halide group, the dinuclear complex is usually formed in stoichiometric amounts. The stability of thiosemicarbazonate specie depends also of ligand nature, so that the thiosemicarbazones derivated from aldehyde give the dimer more easily than those derived from ketones.

Recently, we had tried the synthesis of rhenium(I) complexes of the thiosemicarbazone derived of 4-(dimethylamino)benzaldehyde and we have observed the systematic formation of the dinuclear complex as crystal from solutions of the monomer in several solvents and at different temperatures.

In addition, we have isolated two different compounds depending of the ligands disposition respect to the Re₂S₂ diamond: the centrosymmetric arrangement (Figure 1 left) and the dissymmetric arrangement (Figure 1 right). Both dimers were able to isolated as separated single crystals and also as a co-crystal.

In the present work, we study the structural differences between both kind of structures and we describe the possible factors determining the formation of one or other symmetric disposition.

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Keywords: Dimer, thiosemicarbazone, crystal

Organoruthenium complexes containing allylphosphite ligand

Nuria Álvarez Pazos1

 Departamento de Química Inorgánica, Universidade de Vigo, Vigo, Spain

email: nualvarez@uvigo.es

The reaction of the ruthenium(II) complexes $[RuCp^{\circ}Cl(PPh_{3})_{2}]$ ($Cp^{\circ} = \eta^{5}-C_{3}H_{5}$ or $\eta^{5}-C_{9}H_{7}$) with an excess of allyldiphenylphosphite leads to the neutral complexes $[Ru(\eta^{5}-C_{3}H_{5})Cl(k^{3}(P,C,C)-PPh_{2}OCH_{2}CH=CH_{2})]$ (**1a**), $[Ru(\eta^{5}-C_{3}H_{5})Cl(k^{1}(P)-PPh_{2}OCH_{2}CH=CH_{2})_{2}]$ (**1b**) and $[Ru(\eta^{5}-C_{9}H_{7})Cl(k^{1}(P)-PPh_{2}OCH_{2}CH=CH_{2})_{2}]$ (**2b**). The molecular structure of the new ruthenium complexes **1a**, **1b** and **2a** have been determined by X-Ray diffraction. In the complex **1a** the phosphite ligand is bonded to the ruthenium through the phosphorous and the C-C double bond. On the other hand in compounds **1b** and **2a** he ligand is bonded to the metal centre only through the phosphorous atom.



Figure: Synthesia and structure of complexes to and th

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Keywords: Allylphosphite, ruthenium,

MS36-P05

In situ XRD and EXAFS/XANES study of xCuO-yAl₂O₃-zFe₂O₃ catalyst in reaction of CO oxidation

Olga Bulavchenko¹, Zahar Vinokurov¹, Andrey Saraev¹, Vasily Kaichev¹, Alexander Fedorov¹, Anna Tsapina¹

 Boreskov Institute of Catalysis SB RAS, Novosibirsk State University, Novosibirsk, Russia

email: isizy@catalysis.ru

The Fe-based catalysts have been the subject of intense research in recent decades since wide application in various fields, such as water-gas shift reactions, Fisher-Tropsh synthesis, CO and hydrocarbons oxidation, ammonia synthesis. We are interesting in Fe-based system as effective catalysts for CO oxidation of gasification products of solid fuels in fluidized bed. CO is known to be the main product of gasification of dry fuels (coal, fuel oil, firewood).

One of the ways to stabilize catalyst from sintering, increase surface area and catalytic activity is using various promoters. At the same time, the introduction of different promoters affects the performance of the catalyst, i.e. shifts the temperatures of phase transformations and forms new mixed compounds. These effects strongly depends on the nature and amount of the incorporated metal cation.

We studied the influence of the nature and amount of promoter (A1 and Cu cations) in Fe-O catalysts on the structural, textural, redox and catalytic properties of xCuO-yA l_2O_3 -zFe $_2O_3$ samples in CO oxidation. In this work, we use in situ techniques (XRD and XANES/EXAFS) to study the behavior of catalysts and model systems under reduction in CO. Copper and aluminum can enter into iron oxide during the preparation stage, or during reduction with the formation of a solid solutions based on spinel or hematite structures [1].

Catalytic testing in the CO oxidation revealed the difference in catalytic properties for different modifiers. Catalysts contain Fe_2O_3 , addition of Al atoms leads to a decrease of the oxide crystal size and copper contributes the formation of spinel structure. According to TPR-H₂, Cu addition leads to improvement of reducibility of catalysts and decrease the temperatures of phase transformation.

Usually, reduction of iron oxide involves several steps including the formation of the intermediate oxides such as magnetite and wustite. The reduction of Fe₂O₃ to metallic Fe can be a two-step Fe₂O₃ \rightarrow Fe₃O₄ \rightarrow Fe or three-step Fe₂O₃ \rightarrow Fe₃O₄ \rightarrow FeO \rightarrow Fe mechanisms (depending the temperature and H₂O/H2 ratio) and affected the formation of metastable wustite.

Our in situ study shown that, introduction of aluminum in Fe_2O_3 leads to slowing down the reduction of Fe_2O_3 to Fe_2O_4 and the appearance of reaction products (FeO and Fe) at higher temperatures. The formation of the intermediate solid solution of $Fe_{3-x}Al_xO_4$ and the formation in the reaction products of aluminum-containing spinel-type phases FeA- l_2O_4 and $Fe_{3-x}Al_xO_4$ are also observed. The introduction of Cu has an effect on the acceleration of the stage. FeO \rightarrow FeO, and has little effect on the reduction of Fe3O4 \rightarrow FeO / Fe.

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Keywords: in situ XRD, spinel, catalyst

MS36-P06

Supramolecular dimer of sandwich tripledecker phthalocyaninates studied by single-crystal x-ray diffraction analysis

Anna Sinelshchikova¹, Fedor Dolgushin², Georgy Berezhnoy³, Alexander Martynov¹, Yulia Gorbunova¹-⁴ Aslan Tsivadze¹,⁴

- 1. A.N. Frumkin Institute of Physical chemistry and Electrochemistry RAS, Moscow, Russia
- 2. A.N. Nesmeyanov Institute of Organoelement Compounds of RAS, Moscow, Russia
- 3. Higher Chemical College of RAS, Moscow, Russia
- 4. N.S.Kurnakov Institute of General and Inorganic Chemistry of RAS, Moscow, Russia

email: asinelshchikova@gmail.com

Lanthanide phthalocyaninates with paramagnetic REE(III) ions reveal single-molecular magnetic (SMM) behaviour [1, 2]. The magnetic properties of usual double- or tripledecker sandwich complexes can be tuned by increasing the number of decks. Earlier in our group it was shown that triple-decker phthalocyaninates (1) with one terminal crown-substituted deck is capable for dimerization in solution in the presence of potassium ions [3]. In the present work we proved the formation of such sextuple-decker sandwich complex in solid state by single crystal XRD. The yttrium complex was chosen as diamagnetic reference for later investigations.

The solvates $(1)_2*(KBPh_4)_4\cdot 4(CH_3CN)\cdot 7(CHCl_3)$ were obtained by slow diffusion of KBPh₄ in CH₃CN into the solution of (1) in CHCl₃ at 25 °C. The structural characteristics of the dimer suggest the possibility of the magnetic-dipolar f-f interaction between the ions at M1 and M2 cites, as well as additional weaker coupling between ions at M2 and M2' cites, which can be later observed in the case of isostructural complexes with Tb(III) and Dy(III).

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Keywords: Lanthanide phthalocyaninate, supramolecular dimer, single-crystal XRD

Coordination polymers of group 1 and 2 metals with a dimeric capsular zwitterionic pyridinecarboxylate

Antti Tiihonen1, Manu Lahtinen1

1. Department of Chemistry, University of Jyvaskyla, Jyvaskyla, Finland

email: antti.j.tiihonen@jyu.fi

Coordination polymers with alkali and alkaline earth metals are not unheard of, but those implementing zwitterionic pyridinecarboxylates are very scarce, with only three records in the CCDC database [1-3]. Tripodal zwitterionic pyridinecarboxylate ligand with a systematic name 1,1',1"-((2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene))tris(pyridin-1-ium-4-carboxylate) (TTTPC), forms stable capsular dimers in water by enclosing halides with sufficiently large ionic radius, especially bromide and iodide ($[TTTPC_2X]$). When completely zwitterionic the ligand has neutral net charge, and the enclosed halide ion makes the charge of the capsule one negative. This charge can be balanced by an alkali or alkaline earth metal coordinated to the carboxylate moiety on the outer rim of the capsule forming a 1D polymer with potassium ((K[TTTP- $(C_2X_1)_n$) and a 2D polymer with barium, the 2⁺ charge of the latter metal balanced by an additional halide ((Ba[TTTP- $C_2X|X_{n}$). Both polymers are highly hydrated systems and hydrogen bond networks of water molecules occupy the space between polymeric moieties. Additionally, ammonium as a pseudo-alkali metal functions exactly as potassium. and forms a 0D hydrogen bonded coordination polymer (NH₄[TTTPC₂X]) that mimics the aforementioned 1D polymeric system with an isostructural hydrogen bonded water network. Potassium has a coordination number 7 with four monodentate carboxylates and one bidentate carboxvlate in addition to one coordinated water molecule in its first coordination sphere. Barium has a coordination number 9 with an additional bidentate carboxylate. Potassium system closely assimilates the 2D barium polymer, but must be classified as a 1D polymer, because of the lack of direct coordination to the metal, having only a hydrogen bond to the coordinated water instead. Mean M-O coordination bond lengths of monodentate carboxylates are 2.779 (K) and 2.774 (Ba) angstroms, and bidentate bond lengths respectively 2.896 (K) and 2.894 (Ba) angstroms. All polymers crystallize in the triclinic space group P-1, and their structures have been determined using single crystal X-ray diffraction. Further studies with other metals in similar systems are underway.



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Keywords: Coordination polymers, hydrogen bonding, zwitterions

Copper based Bio-MOFs: Challenges and possibilities in crystal engineering

Marius Kremer1, Ulli Englert1

1. Institute of Inorganic Chemistry, RWTH Aachen University, Aachen, Germany

email: Marius.Kremer@rwth-aachen.de

Metal-organic frameworks present one of the fastest growing categories of structures published in the CCD. Due to their extreme structural and chemical diversity, MOFs can be deployed in many fields of modern chemistry like gas separation, hydrogen storage or catalysis^[11]. Synthesising biologically non-hazardous and medically harmless MOFs provides interesting possibilities for different medical applications like site-targeted drug delivery or medical imaging ^[21] and might be used to replace toxic or hazardous compounds in many other fields. This shift towards a "greener" chemistry is not only potentially beneficial for working conditions and the environmental impact of the industry, but might also lead to an economical benefit, since most reactants used are easy to store, widely available and sometimes even easily recyclable.^[3]

In our experiments, we synthesised coordination complexes from non-toxic copper salts and aspartic acid. Aspartic acid, featuring two carboxylato sites, might enable bridging between multiple copper cations, leading to extended framework structures. Different copper salts were used to synthesise coordination compounds in H₂O and EtOH, the products were then analysed using X-Ray diffraction, IR-spectroscopy and CHN elemental analysis. Since growing single crystals suitable for X-Ray diffraction proved challenging, several different crystallization techniques were employed during the synthesis of the substances.

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Keywords: Bio-MOF, crystal engineering, coordination complex

MS36-P09

Giant organometallic molecular containers

Alexander Virovets1, Eugenia Peresypkina 1, Manfred Scheer1

1. Institute of Inorganic Chemistry, Dept. of Chemistry and Pharmacy, University of Regensburg, Regensburg, Germany

email: avvirovets@yahoo.com

One of the most outstanding and challenging areas in the modern coordination chemistry is the rational design of giant supramolecules built up from metal atoms connected to each other via polytopic organic or organometallic ligands resulting into large hollow cages. During last decade we have been investigating the chemistry of pentaphosphaferrocenes, $[Cp^{R}Fe(\eta^{5}-P_{5})]$ ($Cp^{R} = \eta^{5}-C_{5}R_{5}$, R = Me (Cp^{*}), Me₄Et (Cp^x), CH₂Ph (Cp^{Bn}), PhC₄H₉ (Cp^{BIG})). Being stable in inert atmosphere, these organometallic compounds proved to be very attractive as versatile building blocks for the rational design of giant supramolecules with an inorganic core built up from Cu+ and Ag+ cations coordinated to the phosphorus atoms of the cyclo-P₅ ligands [1-3] (Fig. 1). Varying the nature of R, counterions and synthetic conditions, we obtained, in astonishingly high yields, hollow or multishell supramolecules of 2.1 - 4.6 nm in diameter alongside with the first coordination polymers with such supramolecules as nodes (Fig. 1c,f). Special crystallization techniques allow obtaining the single crystals suitable for the X-ray diffraction study using laboratory diffractometers or synchrotron radiation, which is accompanied by NMR studies in solid state and solution.

The central cavity of the hollow supramolecules (reaching 0.60 – 1.35 nm) can include various guest molecules (Fig. 1). Host supramolecule can often be adjusted to the size, shape and charge of the guest molecule. Thus, we succeeded in encapsulation of metastable molecules of white phosphorus (P₄) and yellow arsenic (As₄), various metallocenes (e.g., Cp₂Fe, Cp₂Ni, CpVC₇H₇) and triple-decker complexes (e.g., [CpCr)₂(η^2 -As₅)] and [(CpMo)₂(η^3 -P₃)(η -PS)]), as well as cage molecules (C₆₀, adamantane, o-carborane, P₄Sa₅) (Fig. 1a-e). The anionic and cationic species also can be encapsulated, like, e.g., the cobaltocenium cation into the negatively charged supramolecule in [CoCp₂]⁺₃{[CoCp₂]⁺@[{Cp*FeP₅}₈Cu₂₄₂₅Br_{28.25}(CH₃CN)₆]₄} [2] (Fig. 1a).

The analysis of the host-guest interactions allowed us to reveal their novel types, namely, $P_5 \cdots P_3$ and $C_5 \cdots P_5 \pi - \pi$ -stacking between the *cyclo*- P_5 ligands of the supramolecular host and Cp*FeP₅ or Cp-containing guest molecules. Usually the guest molecules are disordered, statically or dynamically depending on their nature. Thus, the way of disorder of ferrocene molecule in the central cavity of supramolecular host in [FeCp_2]@[{Cp*FeP_3}_8Cu₁₉₃Br₁₉₃] proved to be temperature-dependent in a range between 5 and 243 K (Fig. 1e).

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Keywords: self-assembly, host-guest compounds, pentaphosphaferrocene

MS36-P10

Modifying the RheManTec Triad – a small molecule meanders into the macromolecular world

Alice Brink1

 N.S.Kurnakov Institute of General and Inorganic Chemistry of RAS, Moscow, Russia Chemistry Department, University of the Free State, Bloemfontein, South Africa

email: brinka@ufs.ac.za

Drug development can be approached from numerous angles especially when including the use of transition metal complexes. The utilisation of structural analysis in small molecules can provide a valuable platform whereby additional functionalization of the model pharmaceutical can be evaluated. Particularly when considering the possible bio-activity and receptor binding of the small molecule. Kinetic and mechanistic studies can further describe the coordination tendencies of the small molecule and is critical for understanding reactivity and stability which may be associated to the structural effects. Furthermore to expand the library of information into a system which realistically mimics a biological environment, structural analysis can be conducted by the combination of the small molecules with proteins in a methodology similar to fragment based drug development.

Our research interest is in the modification of bifunctional chelators coordinated to the tricarbonyl complexes of the group 7 Manganese Triad. Particular interest is focused on the radionuclides of ⁹⁹mtechnetium(I) and ^{180/188}rhenium(I) for their application in diagnostic or therapeutic nuclear medicine. To this end we have meandered our way from a small molecule study, involving the kinetic and crystallographic properties of the *fac*-[M(CO)₃]⁺ core (M = Re, Tc) and crossed over into the world of macromolecular crystallography. The coordination possibilities of multiple amino acid residues to the *fac*-[Re(CO)₃]⁺ complex in a protein is described. Furthermore, the formation of mono-nuclear versus multi-nuclear complexes can be observed in both small molecule and macromolecular studies.

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Keywords: Drug development, rhenium, radiopharmaceuticals

Effect of dehydratation on zinc malonate complexes with 1,2-bis(pyridin-4-yl) ethylene

Ivan Ushakov¹, Alexander Goloveshkin¹, Anna Vologzhanina¹, Ekaterina Zorina-Tikhonova², Aleksandr Chistyakov², Aleksei Sidorov², Igor Eremenko²

 A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Laboratory for X-Ray Diffraction Studies, Moscow, Russia

2. Kurnakov Institute of Inorganic Chemistry, Moscow, Russia

email: f0rbmen@gmail.com

Recently we carried out a series of photoinitiated reactions in zinc malonates with bis(pyrid-4-yl)ethylene [1]. The transformation of $\{[Zn(bpe)(Me_2mal)] \cdot H_2O\}_n$ to $\{[Zn(bpe)$ $(Me_2mal)_2[Zn_2(tpcb)(Me_2mal)_2] \cdot H_2O_n$ (Me_2mal = dimethylmalonate, tpcb = 1,1,2,2-tetrakis(pyridine-4-yl)cyclobutane) was proposed to be affected by dehydratation reaction. Thus, we studied the effect of dehydration on above $\{[Zn(bpe)(Me_2mal)] \cdot H_2O\}_n$ and its isostructural analog { $[Zn(bpe)(cbdc)] \cdot H_2O$ }, (cbdc = cyclobutane-1,1-dicarboxylato). Both compounds were heated for 2 hours at 120°C until constant weight and then irradiated with UV for 8 hours. Transformations of crystalline compounds were controlled by means of powder X-ray diffraction (Figure) and 1H NMR. As it follows from Figure, similarly with {[Zn(bpe)(Me₂mal)] H₂O}, dehydration of {[Zn(bpe)(cbdc)]·H₂O}_n to {[Zn(bpe)(cbdc]}_n and irradiation of the latter compound can be described as a two-stage solid-state process. Based on our data, irradiation of {[Zn(bpe)(cbdc)]·H₂O}_{*n*} at room temperature seem to be accompanied by dehydration. Analysis of the reaction products is underway now.



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Keywords: photoinitiation, complex compounds, X-ray diffraction

MS36-P12

Structural analysis and antimicrobial activity of a new dithiocarbazate and its Copper(II) complex

Francielle Lima1, Thayná Silva2, Carlos Martins2, Claudia Gatto1

- 1. Chemistry Institute University of Brasilia, Franca, Brazil
- 2. Biology Institute University of Franca, Franca, Brazil

email: franci_l@hotmail.com.br

Dithiocarbazates and their metal complexes have been the subject of many studies because they have a wide range of pharmaceutical applications and also because of their chemical and structural versatility.[1,2] These Schiff bases present themselves in their varied structures coordination sites and allow the formation of complexes with several transition metals. Based on our interest in this class of compounds, the present study describe the synthesis and crystallography evaluation of the new ligand 2-hydroxyacetophenone-S-dithiocarbazate (H₂L¹) and its copper(II) complex, [(CuL¹)₂]. The compounds were characterized by elemental analysis and spectral measurements (IR, UV-Vis, 1H NMR and ¹³C NMR). The packing architectures revealed by single crystal X-ray diffraction analysis showed bifurcated intramolecular hydrogen bonds which are responsible for the formation of a dimer-like structure. The ligand adopts an E configuration and tautomeric and thione form. The copper(II) complex is a dimeric structure with a distorted square planar coordination geometry around each copper atom. The metal centers are connected by μ_2 -oxo bridges with ONS-donor ligands. The distance between the metal atoms of is 2.926(6) Å, long enough to have any metal-metal interaction. In addition, the biological properties of the compounds were evaluated against a variety of bacteria and fungi. In all experiments, due the structure and properties of the copper(II) complex was a greater antimicrobial activity observed compared to the free dithiocarbazate.



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Keywords: Crystallography, Dithiocarbazates, Biological Analysis

Novel isostructural and isoeletronic nickel(II) and palladium(II) complexes: Crystallographic and spectroscopic evaluation

Carolane Almeida1, João Guilherme Carvalho2, Claudia Gatto1

- 1. Chemistry Institute / University of Brasília, Brasília, Brazil
- 2. Technische Universität München, Munchen, Germany

email: macedo.carolane@gmail.com

Metal complexes with biologically important ligands have received a great attention in the last decades. The thiosemicarbazones and their complexes it is a permanent fiel of research due the numerous pharmacological properties and applications, with anticancer, bactericidal and fungicidal activity.[1] The activity of the coordination compounds of transition metals is normally increased compared to the free thiosemicarbazones and depends largely on their structure and properties.[2] So the crystallographic elucidation of these compounds is important and fundamental to evaluate their possible applications. We describe the synthesis of two new complexes, [Ni(L)Cl] (1) and [Pd(L)Cl] (2), with the ligand 2-acetylpyridine N4-phenylthiosemicarbazone (HL). The compounds have been characterized by elemental analysis and spectral (IR, UV-Vis, 1H NMR, and 13C NMR) measurements. Crystal and molecular structures of both complexes have been determined by single crystal X-ray analysis. It was found that the ligand coordinates with tridentate NNS donor atoms, in its deprotonatd tiona form. The chlorine ion is present in the coordination sphere for the both center atoms of the complexes, with Ni-Cl distance of 2.163(10) Å and Pd-Cl of 2.298(8) Å and displays the square-planar geometry with significantly distortion. The compounds are isoeletronic with d8 configuration and isostrutctural, also observed at spectroscopy analyses. Interestingly, the intermolecular hydrogen bonds have also been observed in both complexes and are responsible for the formation of a dimer-like structure in the crystal structure. For the purpose of complexation, all the techniques employed were compared with results obtained for the complex agent, and thus, to study with more clarity the influence of the metals in the structure, stability and property of these ligands. The biological potential applications of the compounds have been studied against cancer cells.



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Keywords: hydrogen bons, dimer, transition metals

MS36-P14

Structurally diverse of [Mn(salen)(NCS/ NCSe)] complexes

Jan Moncol1, Martin Schoeller1

 Institute of Inorganic Chemistry, Technology and Materials, Slovak University of Technology in Bratislava, Bratislava, Slovakia

email: jan.moncol@stuba.sk

Manganese(III)-salen complexes are subject of three research studies: (i) the design of models of Mn-containing proteins and enzymes, (ii) the development of catalysts for oxidations of organic substrates, and (iii) study of magnetism of Mn(III) complexes. Manganese(III)-salen complexes are interesting synthetic systems that can act as mimetic of catecholase, peroxidase, catalase and superoxide dismutase [1-3].

In this study, a series of thiocyanate- and selenocyanate- manganese(III) complexes derived from Schiff based obtained by the condensation of salicylaldehyde, 5-bromo-salicylaldehyde, 5-chloro-salicylaldehyde, 3,5-dibromo-salicylaldehyde or 3,5-dichlorosalicylaldehyde and 1,2-diamineethane have been synthesized and characterized using single-crystal X-ray crystallography in the cases of [Mn(3,5-Br₂salen)(µ-NCS)]_n (1), [Mn(3,5-Br₂salen)(µ-NCSe)] [Mn(3,5-Cl₂salen)(µ-NCS)] (2), $_{n}$ (3), [[Mn(3,5-Cl_{2}salen)(μ -NCSe)] $_{n}$ (4), [Mn(5-Cl_{3}salen) $(\mu$ -NCSe)]_n.nMeOH (5), [Mn(5-Brsalen)(NCS)]₂ (6), $[Mn(5-Clsalen)(NCS)]_2$ (7) and $[Mn(5-Brsalen)(NCSe)]_2$ (8). The complexes 1-5 form 1D coordination polymers with thiocyanate or selenocyanate bridging ligands. The compounds 2, 4 and 5 are first examples of manganese(III) complexes with bridging selenocyanate ligands. The compounds 6-8 are dinuclear molecular complexes with terminal thiocyanate or selenocyanate ligands.



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Keywords: Coordination polymer, Mn(III)-salen, Crystal structure

Synthesis, structural and characterization of three barium aromatic coordination polymers displaying a hydrogen-bonded layer structures

Balegroune Fadéla¹, Assia Djeghri¹, Aouaouche Benkanoun¹, Slimane Dahaoui²

1. Laboratoire CRI-THER, Faculté de Chimie, USTHB, lger, Algeria

 CRM2, UMR 7036 CNRS, Université de Lorraine BP70239-54506, Vandœuvre-lès-Nancy, France

email: fbalegroune@yahoo.fr

Coordination polymer materials have been demonstrated to have excellent properties and potential applications such as catalysis, magnetic, optical materials, gas adsorption, antibacterial agents, antitumor drugs, and so on [1-2].

Our research interest has been focused on a systematic study of coordination polymers based s-block alkaline-earth metal ions and organic diacids [3]. In this paper, we reported the synthesis and characterization of three Ba coordination polymers from1,2-benzene-dicarboxylic acid [Ba(H₂O)(OOC-C₆H₄-COOH)₂], 2,2'-biphenyldicarboxylic acid [Ba(OOC-(C₆H₄)₂-COO)(H₂O)₄] 0.25 H₂O and 1,4-butanedicarboxylic acid (adipic acid) [Ba(OO-(CH₂)₄-COOH). The three compounds crystallise in space groups P2₁/c Pcan and P-4b2 respectively.

The structure of the first complex is built up from polymeric aquabis(hydrogeno-*o*-phthalate)barium(II) units. Each barium(II) binds to ten O-donors atoms, eight of which belong to six symmetry-related [HBDC] ligands and the remaining two to two water molecules. Thus, the coordination geometry around the Ba(II) atom can be best described as a distorted bicapped square antiprism. In such a way, the complex units are assembled into a two-dimensional infinite layer structure parallel to the (001) plane. The inorganic barium-oxygen layers are generated from Ba_2O_{20} units which share faces and edges with neighbours to form chains along the [010] and [100] directions, respectively.

For complex $[Ba(OOC-(C_6H_4)_2-COO)(H_2O)_4] 0.25 H_2O$, the Ba (II) ions are ten-coordinated with three carboxylate oxygen atoms and with seven oxygen water molecules. Therefore, the coordination geometry around Ba(II) ions can be described as distorted bicapped dodecahedra. Its coordination architecture is built up from two-dimensional inorganic sub-networks made from face-sharing ten-coordinated Ba(II) polyhedra connected by the 2,2'diphenate linkers. Strong hydrogen bonds involving all the coordinated water molecules and the O atoms of the carboxylate groups lead to the formation of a three-dimensional network.

In the last complex, the asymmetric unit consists of one Ba(II) cation lying on -4 axis and one half dicarboxylate ligand. The barium is eight-coordinated by eight oxygen atoms belonging to eight equivalent dicarboxylato ligands. The coordination geometry around the Ba(II) can be best described as a distorted bicapped trigonal prism. The adipate ligands are tetradentate with syn/anti conformation. The structure is built up from chains of isolated polyhedra BaO₈ running parallel to [100] axis which are further connected through bridging dicarboxylate anions and separated by an infinite array of alkyl chains into 3D structure.

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Keywords: Barium, Structure, PCs

A new double metal oxalate compound with specific structural features

Malika Hamadene¹, Hamza Kherfi¹, Fadila Balegroune¹

1. Laboratoire CRI-THER, Faculté de Chimie, USTHB, Alger, Algeria

email: mal_hamadene@hotmail.com

Only a very few examples of double oxalate compounds with Li have been reported in the litterature [1,2]. In continuation of our crystallographic research about the coordination compounds [3], we have chosen to focus on mixed oxalate with Li atoms and 3d element. Pink single crystals with the Cr element have been obtained. Optical, thermal and RX analysis have lead to the formula $[LiCr(C_2O_4)_2(H_2O)_4]$ _n and space group C_2/m . In this structure, both metal atoms in special positions are coordinated to two equivalent water molecules in axial sites and four equivalent O atoms from coplanar oxalate groups. The crystal structure consists of infinite and linear chains of trans-Cr(O2)4(Ow2)2 and trans-Li(O1)₄(Ow1)₂ octahedra µ₂-bridged by oxalate groups, and propagating along [101] direction. The Ow1 atoms around the Li atom are disordered over two positions separated by 0.5259 (6) Å, due to the wagging in the (101) mirror plane. Taking into account of the 2/m imposed symmetry of both metallic elements, the unit cell may be described as an unconventional pseudo face-centered monoclinic cell. In this one-dimensional coordination polymer, $R_4^4(12)$ H rings are present between the parallel chains to stabilize a 2D framework. The UV and IR analysis are agreeing respectively with the trans conformation of Cr (III) octahedral due to the lack of the ruby line and the symmetry of the bridged ligands. The investigated compound is found to be a precursor of a ternary oxide LiCrO2 deducted from the thermal analysis.

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Keywords: 1D polymer ; O atoms disorder ; H rings

MS36-P17

Further Structural Adventures with Bismetallacarboranes

Georgina Rosair¹, Alan Welch¹, Anthony Chan¹

1. Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, United Kingdom

email: g.m.rosair@hw.ac.uk

Metallacarboranes display great variation in polyhedral size and shape. They incorporate metal atoms from across the Periodic Table¹ and find application in catalysis, medicine, metal-ion extraction and advanced materials.¹

The parent 1,1'-bis(*ortho*-carborane) (below) has a scaffold which offers extensive potential for derivatisation. Single cage metalation of 1,1'-bis(*ortho*-carborane) has yielded metallacarborane-carborane species,² with double cage metalation affording metallacarborane-metallacarborane compounds.² However such metalation follows double deboronation (removal of one vertex from each cage) so the final products are necessarily homometalated. Very recently stepwise deboronation and metalation of 1,1'-bis(*ortho*-carborane) has enabled the synthesis and characterisation of the first examples of heterometalated metallacarborane-metallacarborane species (one example below). More variety and surprises are revealed in this structural adventure with metallacarborane.³



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Keywords: Carboranes, cages, isomerisation

Crystal Structure and DFT calculations of (6*E*)-6-({[2-methoxy-5- (trifluoromethyl) phenyl] amino} methylidene)-4- nitrocyclohexa-2,4-dien-1-one

Ahmet Erdönmez¹

1. Retired, Samsun, Turkey

email: ahmeterdonmez52@gmail.com

The crystal structure of (6E)-6-({[2-methoxy-5-(trifluoromethyl)phenyl]amino}methylidene)-4-nitrocyclohexa-2,4-dien-1-one (C15H11F3N2O4) has been determined by means of single-crystal X-ray diffraction methods. The title compound C15H11F3N2O4 is a Schiff base that adopts the ketol-amine tautomeric form in the solid state. Whole molecule is nearly planar with dihedral angle 6.19(10)° between the aromatic rings. The title compound crystallizes in the trigonal space group R-3 with the unit cell parameters: a=33.0238(17), b=33.0238(17), c= 7.1144(4)Å, α=90, b=90, γ =120 (°), V= 6757.1(8)Å³, Z=18. The molecular structure is stabilized by two N-H...O type intramolecular H bond, two C-H··O type intermolecular hydrogen bonds and a N-O... π and five π - π interactions. X-ray measurements was carried out on a STOE IPDS II diffractometer with MoK_a radiation. The molecular structure was solved by direct method using SHELXS-97 and refinement by full-matrix least-squares on F² using SHELXL-14 program. An ortep-3 view of the molecule of title compound is shown in Fig.1.



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Keywords: Schiff base, Single-crystal, X-ray diffraction, Schiff base, Keto-amine, Crystal structure, DFT calculations.

The mononuclear MoO₂²⁺ complexes with stereochemically rigid 4-aminobenzhydrazide based ligands

Gordana Pavlović¹, Danijela Cvijanović², Jana Pisk³, Marina Cindrić³, Višnja Vrdoljak³

- 1. University of Zagreb, Faculty of Textile Technology, Zagreb, Croatia
- University of Zagreb, School of Medicine, Department of Chemistry and Biochemistry, Zagreb, Croatia
- University of Zagreb, Faculty of Science, Department of Chemistry, Zagreb, Croatia

email: gpavlovic@ttf.hr

A range of dioxidomolybdenum(VI) complexes has displayed very high catalytic activities and exquisite selectivity. The dioxidomolybdenum(VI) mononuclear complexes with 4-aminobenzoylhydrazone ligands (salicylaldehyde (H2L1), 3-methoxysalicylaldehyde (H2L2), or 4-methoxysalicylaldehyde 4-aminobenzoylhydrazone (H₂L³) being of the type cis-[MoO₂L¹⁻³(D)]; D = MeOH, EtOH, H₂O, dmf] have been prepared and structurally characterized. The crystal structure analysis of mononuclear complexes (Fig.1.) reveals distorted octahedral Mo(VI) coordination by ONO donor atoms from dianionic tridentate 4-aminobenzoylhydrazone ligands, two oxido oxygen atoms from the MoO22+ moiety and the oxygen atom from coordinated alcohol molecules (D = MeOH, EtOH). The molybdenum oxido groups of the MoO22+ moiety show the expected mutual cis configuration and are located trans to the imine nitrogen atom and coordinated alcohol molecule. The bond distances range around Mo follows trend: Mo-Ot < Mo-O(phenolate) < Mo-O(hydrazone part) < Mo-N< Mo-O(ROH; R=Me, Et). The bicyclic system of two chelate rings is slightly folded along the axis of molybdenum-imino bond and by the offset of metal centre apart from chelate planes towards the terminal oxygen atom. The most deviation from chelate rings coplanarity is shown by the phenolate oxygen atom due to its participation in intermolecular interactions. The complexes were tested for catalytic epoxidation of cyclooctene under eco-friendly reaction conditions by using aqueous tert-butyl hydroperoxide (TBHP) as an oxidant. Due to trans effect of oxido oxygen atom, Mo-O(D) bond is the longest bond distance within molybdenum coordination sphere and it expected to be the point of maximum catalytic reactivity of the complexes. It is previously shown that pentacoordinated molybdenum systems activate oxidizing agent TBHP through adduct formation assisted by the O-H-O hydrogen bond. Another explanation of the substituent influence is $p - \pi$ conjunctive effect with methoxy group due to increasing electron density of the phenyl ring.

MS36-P20

Crystal structure and thermal and mechanical properties of a herringbonetype Cu^{II}-based solid coordination framework

Gotzone Barandika¹, Francisco Llano-Tomé², Begoña Bazán²-³, Miren Karmele Urtiaga², María Isabel Arriortua²-³

- 1. Química Inorgánica, Universidad del País Vasco (UPV/EHU) and BCMaterials, Leioa, Spain
- Mineralogía y Petrología, Universidad del País Vasco (UPV/ EHU), Leioa, Spain
- BCMaterials, Universidad del País Vasco (UPV/EHU), Leioa, Spain

email: gotzone.barandika@ehu.eus

Solid coordination frameworks (SCF) represent one of the most studied materials during the last decade thanks to the variety of structures that can be formed by using metal complexes as synthons.1 In fact, combination of polycarboxylate anions and dipyridyl ligands is an effective strategy to produce SCF compounds, and we have previously reported on Cu^{II}-based SCFs exhibiting PDC (2,5-pyridinedicarboxylate) in combination with bpe (1,2-di(4- pyridyl)ethylene)), bpa(1,2-di(4-pyridyl)ethane), and dpk (di-2-pyridyl ketone). The use of bpe and bpa as dipyridyl ligands produces 3-connected herringbone structures, and so far our main contribution to the study of this type of structures consists on the identification of two types of herringbone arrays (4-c and 3-c where c stands for "connected") depending on the number of connections for each metal node. While M1A1B1 stoichiometry corresponds to 4-c arrays, M2A2B stoichiometry corresponds to 3-c ones (M is the metal ion, and A and B are the organic ligands). Additionally, we also identified the structural parameters defining the 3-c herringbone arrays and observed a correlation between angles and distances in this type of structure.

In this context, this work is focused on the synthesis and characterisation of the compound [Cu₂(PDC)₂(4,4'-bipy) (H₂O)₂]-MeOH (where 4,4'-bipy is 4,4'-bipyridine and MeOH is methanol) with the aim of studying the influence of distinct dipyridyl ligands on the as-obtained characteristics materials. The compound crystallises in the monoclinic system (P 2₁/n, a=11.3583 Å, b=9.2348 Å, c=12.6150 Å, B=102.254°). Thermogravimetric analysis reveals that it is stable up to 280°C. Nanoindentation experiments on single crystals produced values of the E Young modulus between 1.325 GPa and 9.860 GPa, and values of the hardness between 0.030 GPa and 0.401 GPa depending on the crystal face.



Keywords: molybdenum complexes, 4-aminobenzoylhydrazone ligands

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Keywords: CuII-based SCF; herringbone 2D-structure, nanoindentation

MS36-P21

New route to double perovskite oxides using the mixture of oxalate precursors

Marijana Jurić¹, Jasminka Popović¹, Lidija Androš Dubraja¹, Filip Torić², Damir Pajić²

- 1. Ruđer Bošković Institute, Zagreb, Croatia
- 2. Department of Physics, Faculty of Science, University of Zagreb, Zagreb, Croatia

email: Marijana.Juric@irb.hr

Properties of the mixed-metal oxides could be highly affected by the effect of crystallinity, particle size, phase composition and morphology. These can be tuned in part by changing the synthesis methods.

The possibility of using metal-organic coordination systems through the thermal decomposition process as molecular precursors in the synthesis of nanomaterials with high surface and specific morphology has been considered only recently. It has been observed that the use of a well-defined heterometallic precursor can produce crystalline oxide materials under conditions that are significantly milder than those applied in traditional solid-state synthesis. Also, the single-source precursors provide better control over the stoichiometry of the metal ions in the final products as well as the homogeneity of the materials due to the mixing of the metals at the molecular level. The existence of bridging or chelating ligands in the precursors prevents metal separation during oxide formation. For example, the C₂O₄²⁻ anion easily decomposes to the vapour phases CO2 and CO, by the low-temperature routes, and hence, heterometallic oxalate complexes are very convenient for the preparation of mixed metal oxides.[1]

Most of the perovskite compounds that have potential technological interests are not simple systems, but rather ternary oxides such as $A(B^*B^*)O_3$. Heterometallic oxalate complexes do not always contain the appropriate stoichiometry for the formation of the desired single phase oxide. So, we have tested whether the multimetallic oxides containing two or more metals could be prepared by mixing two or more different oxalate precursor in various ratios prior to thermal decomposition.^[2]

A highly crystalline materials $Ba(M_{1/3-x}M_x'Nb^{\vee}_{2/3})O_3$ (M = Ni^{III}, M' = Co^{III}; x = 0-1/3] were obtained after thermal decomposition of the mixture of the well-defined and structurally characterized heterometallic oxalate-based compounds $Ba_2(H_2O)_5[NbO(C_2O_4)_3]HC_2O_4$; $H_2O_1^{II}$ [Ni(bpy)₃]₂[N-bO(C_2O_4)_3]C1:12H_2O_1^{IJ} and [Co(bpy)₃]₂[NbO(C_2O_4)_3] c1:12H_2O_1^{IJ} grinded in an agate mortar in different ratios.

The phase formation and structural ordering of the tri- or tetrametallic perovskite oxides obtained by this modified molecular precursor route have been characterized by powder X-ray diffraction, scanning electron microscopy and energy-dispersive X-ray spectroscopy. The magnetic properties of newly prepared materials which adopt the disordered cubic structure (with random distribution of *B* and *B* "ions) have been also investigated.

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Keywords: mixed-metal oxides, molecular oxalate precursors, thermal decomposition

Using pressure to enhance the magnetic exchange interactions within Cr(III) dimers

Helen Duncan¹, Simon Parsons¹, Euan Brechin¹, Gopalan Rajaraman², Hector Fraser¹

- 1. School of Chemistry, University of Edinburgh, Edinburgh, United Kingdom
- Department of Chemistry, Indian Institute of Technology Bombay, Mumbai, India

email: h.duncan@ed.ac.uk

We have investigated a large series of Cr(III) dimer complexes with general formula $[Cr_2(Me-deaH)_2(O_2CR)Cl_2]_2$. In these materials, magnetic properties are determined by highly deformable intermolecular interactions. The carboxylate above the Cr2 moiety distorts the planarity of the $[Cr_2O_2]$ unit, promoting a net ferromagnetic exchange between the metals.

Through substitution of R with eight organic groups, and DFT calculations the key structural contributions to the net exchange, which has both anti- and ferromagnetic contributions, have been identified. The key contributions are the out of plane angle, θ , the Cr—O—Cr angle, ϕ , and the distortion of the planarity of the [Cr₂O₂] unit, ψ (Figure 1a, b, c respectively). [1]

We now use pressure to drive these structural transformations in three dimers where R = Me (acetate), tBu (pivalate) and Ph (benzoate); a method which has previously successfully been used to enhance the magnetic exchange in Re(IV) molecular magnets. [2] Through applications of pressures up to 4.6 GPa, we have increased θ by up to 5.1(6) ° and ψ by up to 1.4(2) °, (Figure 1d) which was predicted to increase the ferromagnetic contribution and decreased ϕ by up to 2.0(4) ° which was predicted to increase the *antiferromagnetic* contribution.

Considering both the pressure-induced structural deformations, and the ambient pressure DFT we have predicted the optimum pressures to enhance the ferromagnetic exchange in these dimers, and compared the predictions against high-pressure magnetic susceptibility measurements.



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Keywords: High-pressure, Magnetism, Chromium

Pore engineering through the supramolecular modification of Mo-based metallocycles: from 0D discrete cavities to 1D open channels

Eleni C. Mazarakioti¹, Javier Lopez Cabrelles¹, Guillermo Minguez Espallargas¹

1. Instituto de Ciencia Molecular (ICMol), Universitat de Valencia, Valencia, Spain

email: eleni.mazarakioti@uv.es

The synthesis of novel crystalline discrete molecular materials combined with interesting supramolecular architectures providing porosity still consists one of the challenges in synthetic coordination chemistry. The forming cavities, resulting from the *coordination driven self-assembly* of the clusters, play a crucial role in the *host-guest recognition properties* with diverse applications in catalysis, adsorption, drug delivery *etc.*¹ Moreover, any crystal-packing modification can significantly differentiate the physical properties of the solid-state material.² Although network materials are representative examples of crystalline porous materials, discrete molecular compounds have shown a tendency to a more close-packing supramolecular assemblies. To this end, research efforts have been devoted to the development of new coordination clusters displaying permanent porosity.³

Herein we present the syntheses of two structurally similar Mo-based metallocycles with different supramolecular structures. The replacement of the terminally bound pyridines of the initial cluster by the 1,3-di(4-pyridyl)propane forced the metallocycles to reorient their positions yielding a crystal-packing architecture with well-defined channels within the compounds (see Figure). Fully chemical and physical characterization of both complexes is also discussed.

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Keywords: Metallocycles, Porosity, Molybdenum

MS36-P24

Topological analysis and properties of new imidazole-based systems as potential candidates for biological applications

Amani Direm¹, Mohammed S. M. Abdelbaky², Koray Sayın³, Andrea Cornia⁴, Olufunso Abosede⁵, Santiago García-Granda²

- Laboratoire des Structures, Propriétés et Interactions Interatomiques LASPI2A, Département des Sciences de la Matière, Faculté des Sciences et de la Technologie, Université 'Abbes Laghrour', Khenchela 40.000, Algeria, Khenchela, Algeria
- Departamento de Química Física y Analítica, Universidad de Oviedo – CINN, 33006 Oviedo, Spain, Oviedo, Spain
- Department of Chemistry, Faculty of Science, Cumhuriyet University 58140 Sivas, Turkey, Sivas, Turkey
- Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia & INSTM, via G. Campi 103, 41125 Modena, Italy
- Department of Chemistry, Federal University Otuoke, P.M.B 126, Yenagoa, Bayelsa State, Nigeria, Yenagoa, Nigeria

email: d amani 83@yahoo.fr

Transition metal complexes based on imidazole have shown significant interest in biological systems, especially carboxylate mixed-ligands systems of copper(II), which display a variety of pharmacological effects, including antitumor, superoxide dismutase and catecholase activities [1]. Despite the considerable number of the reported imidazole systems built of different carboxylate ligands and metallic centers, namely : copper, cobalt, nickel, manganese, cadmium and ruthenium, the crystallographic information about imidazole-based copper(II) complexes containing citrate mixed-ligands is rather rare, except for only two hexacoordinated complexes of cobalt and nickel [2]. In order to contribute to the well-understanding of these systems, the one-pot synthesis, the crystal structure, the properties and the topological nets of two copper(II) potential candidates for biological applications involving imidazole and citrate mixed-ligands were reported [3].

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Keywords: Imidazole-based systems, topological analysis, biological properties

Structures and physical properties of some derivatives of 2,2';6',2"-terpydine chelating Fe/Co metal complexes

I-Jui Hsu¹, Yan-An Chen¹, Ming-Jing Hsu¹, Yu-Chun Chuang², Jey-Jau Lee², Jyh-Fu Lee²

- 1. Institute of Organic and Polymeric Materials, Taipei, Taiwan
- 2. National Synchrotron Radiation Research Center, Hsinchu, Taiwan

email: ijuihsu@mail.ntut.edu.tw

The muti-functional metal complex with magnetic, luminescence, or conductivity properties is one of the directions to design new modern materials. Spin crossover (SCO) compound is one kind of these complexes due to its potential applications to sensors, information storage, cantilever and so on. In this work, we modify terpyridine to 4'-(2-Furyl)-2,2';6',2"-terpyridine (ftpy) and 1-methyl-1H-Pyrrol-2-yl-2,2';6',2"-terpyridine (mtpy), and successfully obtained metal complexes $M(II)L_2(BF_4)_2$ (M = Fe(II), Co(II); L = ftpy, mtpy). In these metal complexes, Co(II)(ftpy)₂(BF₄)₂·1.5H₂O (complex 1) exhibits SCO behavior from high spin (HS) state with $\mu_{eff} = 4.10$ B.M. at 350K to low spin (LS) state with μ $_{\rm eff}$ = 2.14 B.M. at 100K, but $Co(mtpy)_2(BF_4)_2$ (complex 2) only displays HS state. The other Fe(II) complexes both exhibit diamagnetism. To resolve how structure variation leads to the SCO phenomenon so that we can realize why complex 1 exhibits SCO character, the temperature dependent powder x-ray diffraction (PXRD) measurements are carried out at TPS09A beamline and the high resolution PXRD data are analyzed by Rietveld refinement to obtain detailed structural information. The results indicate that the crystal structures are still in triclinic system from 90K (LS) to 350K (HS) with averaged Co-N distance varied from 2.02(3) Å to 2.10(1) Å. Taking insight into crystal packing structure, one H2O is located at ~ 2.41 Å away from one of furan in complex 1, but no solvent molecule in complex 2. This short distance may indicate intermolecular interaction plays a critical role in tuning SCO phenomenon. In addition, the temperature dependent of x-ray absorption spectroscopy (XAS) is applied to study the electronic structures of complex 1. Moreover, the UV absorption and photoluminescence characters of ftpy and mtpy are also discussed in this study.

Keywords: PXRD, XAS, spin crossover

MS36-P26

Unexpected long-lived photogenerated High-Spin phase investigated by X-ray diffraction

Celine Besnard¹, Teresa Delgado², Antoine Tissot³, Laure Guénée¹, Andreas Hauser², Francisco Javier Valverde-Muñoz⁴, José Antonio Réal⁴, Yu Wang⁵, Sébastien Pillet⁶

- 1. University of Geneva, Laboratoire de Cristallographie, Geneva, Switzerland
- 2. University of Geneva, Physical Chemistry, Geneva, Switzerland
- Ecole Normale Supérieure, Institut des Matériaux Poreux de Paris, Geneva, France
- Departament de Química Inorgánica. Institut de Ciència Molecular (ICMol), Universitat de València, Valencia, Spain
- 5. National Taiwan University, Taiwan
- Laboratoire de Cristallographie, Résonance Magnétique et Modélisations, Université de Lorraine, Vandoeuvre-les-Nancy, France

email: celine.besnard@unige.ch

Spin crossover compounds are interesting photoswitchable materials, with possible applications in sensing or memory devices. At low temperature the Low-Spin state can be excited into the photoexcited High-Spin state through the Light-Induced Excited Spin-State Trapping (LIESST) effect. The relaxation time is however usually short at higher temperatures.

The spin-crossover compound $[Fe(n-Bu-im)_3(tren)](PF_6)_2^{-1}$ shows an unusual long relaxation time at 80K of 20 hours after Light-Induced Excited Spin-State Trapping when irradiated at 80 K. This is more than 40 times longer than the 80K relaxation time when irradiated at 10 K. To explain this unusual behavior single crystal structures were determined after irradiation at low temperature and at 80K. The structures of the two excited High-Spin states differ in the configuration of the side alkyl chains of the compound. Using synchrotron radiation, the long relaxation at 80K could be monitored by single-crystal X-ray diffraction. We showed that the rearrangements of the alkyl chains, which undergo order-disorder transitions, are responsible for the unexpected long relaxation time.

These results highlight the importance of structural studies to better understand and control the LIESST photoexcited states. Multimetastability can be exploited to tune the properties of the system.



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Keywords: Photoswitcable materials, Spin Crossover, structure

MS36-P27

Halogen bonding, actinide contraction and coordination modes of ligands in uranyl, neptunyl and plutonyl trichloroacetates with ammonium cations

Anton Savchenkov¹, Andrei Uhanov¹, Mikhail Grigoriev², Aleksandr Fedoseev², Denis Pushkin¹, Larisa Serezhkina¹, Viktor Serezhkin¹

- 1. Samara National Research University, Samara, Russia
- Russian academy of sciences A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Moscow, Russia

email: anton.savchenkov@gmail.com

Uranyl, neptunyl and plutonyl ions usually form series of isostructural compounds. This fact is very favorable for investigation of the relationship between composition, structure and properties, since it is possible to obtain series of compounds with single varying parameter, for example, the actinide atom, the ligand or the counterion.

In order to obtain new series of U, Np, Pu compounds, we attempted to use trichloroacetate ions as ligands. As a result, single crystals of isostructural compounds (NH₄)₄AnO₂(tca)₆(Htca)(H₂O)₃ (where An is U, Np or Pu and tca is a trichloroacetate ion) were grown and studied using X-ray diffraction analysis. These compounds are of great importance for studying actinide contraction as well as halogen bonding. For example, it has recently been shown that bonds involving halogen atoms can serve as synthons in the formation of supramolecular architectures as well as chemical bonds in the presence of secondary metal atoms in uranyl carboxylate complexes [1]. Halogen bonds in the title crystal structures were analyzed using the method of molecular Voronoi-Dirichlet polyhedra. Actinide contraction in the row of hexavalent U, Np and Pu atoms is discussed on the example of all available series of isostructural compounds.

Aspects of theoretical crystal chemistry are also discussed in the current project. With an increase in the number of structurally studied coordination compounds, it becomes necessary to systematize them in order to facilitate the search for analogous structures, their comparison and identification of common trends in coordination chemistry. One of the methods of description and systematization of complex compounds is the use of crystal-chemical formulae (CCF) [2]. With the help of CCF it is possible to describe any mono- and polynuclear, as well as homo- and heteroligand complexes. CCF's are concise and can be recorded and used automatically by computer algorithms. However, the discussion of halogen-substituted organic ligands in the title compounds required an additional improvement of the recording of CCF and of coordination modes of ligands. In the course of this project, we analyzed coordination modes of trichloroacetate ions in all compounds from CSD [3], what is of great importance for crystal structure prediction and crystal design.

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Keywords: halogen bonding, actinide contraction, coordination modes
Bimetallic coordination compounds based on Al(acacCNen)₃: a building block between inertness and lability

Khai-Nghi Truong¹, Alexander Nellessen ¹, Helena Crützen¹, Hans Gildenast¹, Justin Lange¹, Hassan Osseili¹, Lynn Ferres², Ulli Englert¹

- 1. Institute of Inorganic Chemistry, RWTH Aachen University, Aachen, Germany)
- 2. Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany

email: khai.truong@ac.rwth-aachen.de

Nitrous oxide, N₂O, is an important greenhouse gas and responsible for a significant part of anthropogenic ozone depletion. Searching for suitable catalytic-active materials for its decomposition to the elements is popular. In 2016, Englert and co-workers have reported an attractive Yb₂O₃/ Ag-system which exhibits catalytic activity towards the decomposition reaction of nitrous oxide at 500 °C (commercially-available catalyst: 600 °C).^[1] However, the laborious successive syntheses of the organic ditopic ligand, its Yb complex, and the mixed-metal polymer only allow proof-of-principle studies and preclude any industrial application.^[2] The aim of the current project is the modification and optimization of the synthetic restrictions by using rather unexplored alternative *N*-substituted acetylacetone ligands.

The ditopic ligand 4-acetyl-5-oxohexanenitrile, HacacCNen, exists as enol tautomer in the solid state. The ethyl bridge between the acetylacetone and the nitrile moiety imparts flexibility, which can lead to high degrees of conformational freedom and, thus, interesting structures. The enol form has been experimentally established in the crystal and in solution – how about the geometry of the molecule in the gas phase? Quantum chemical calculations were carried out to answer this question.

In addition, we report two compounds starting from an aluminum(III) complex, $[Al(acacCNen)_3]$, with properties in-between inertness and lability. Depending on the reaction partners and solvent systems, partial degradation or inclusion of the building block as synthesized may occur. In case of a partial degradation when the complex reacts with AgPF₆ in benzene/methanol, an alkoxo-hydroxo-bridged multinuclear Al/Ag cluster is formed. The reaction of the Al(III) building block with silver perchlorate in benzene/ acetonitrile reveals an interesting 1D cross-linking network with inert building block.



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Keywords: Coordination chemistry, extended bimetallic structures, ditopic ligand

1D and 2D porosity in monomeric copper(II) complexes with 1-piperidineacetic acid and 1-piperidineacetamide

Biserka Prugovečki¹, Darko Vušak¹, Neven Smrečki¹, Dubravka Matković-Čalogović¹

1. Department of Chemistry, Faculty of Science, University of Zagreb, Zagreb, Croatia

email: biserka@chem.pmf.hr

1-piperidineacetic acid (HPAA) and 1-piperidineacetamide (HPAAM) can be treated as N-alkylated glycine and N-alkylated glycinamide. N-alkylated amino acids and their derivatives can find application as synthetic building blocks and play an important role in studies related to the structural properties and biological activity [1], [2]. Copper(II) complexes with amino acids and their derivatives were shown to be very interesting compounds for various fields of research, such as bioinorganic chemistry, medicinal chemistry and crystal engineering. Due to versatile noncovalent interactions, these complexes have the ability to form porous structures, coordination polymers, or other different architectures in the solid state [3]. Interestingly, only a few bis(N,N-dialkylamino acidato)copper and bis(N,N-dialkylamino acetamidato)copper complexes have been structurally characterized until now.

In this research we have synthesized and structurally characterized one ligand, HPAAM (1), two copper(II) complexes [Cu(PAA)₂(H₂O)]·3H₂O (2) and [Cu(PAAM)₂]·3H₂O (3), and a sodium salt [Na(PAA)(µ-H₂O)₄(H₂O)]·H₂O (4). Although the only difference between the ligands is the presence of either the carboxylic or the amide group, the influence on the supramolecular architectures of the copper(II) complexes is significant. In 2 a square-pyramidal complex is formed with two O,N-donating PAA ligands in the basal plane and a water molecule occupying the apical position. The molecules are connected into a 2D network through hydrogen bonds. 1D infinite channels of water molecules are formed (Fig. 1a). On the other hand, 1-piperidineacetamide forms a square-planar copper(II) complex hydrogen bonded into a 3D network with 2D infinite channels of water molecules (Fig. 1b). Both copper complexes exhibit trans-coordination, which is not as common in this type of complexes as the cis- coordination, probably due to bulky hydrophobic ligands. 1-piperidineacetic acid crystallized from an aqueous solution as a sodium salt forming a 2D coordination polymer 4 with sodium ions.

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Figure 1. a) 1D channels of water molecules in structure of 2; b) 2D channels of water molecules in structure of 3. Hydrogen atoms are omitted for clarity.



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Keywords: copper(II) complex, N,N-dialkylamino acid, porous crystal structure

Enhancing experimental exploration space with greater dimensions in modern printing

Jake Musselle-Sexton1, Jake Musselle-Sexton1, Michael Probert1

1. School of Natural and Environmental Sciences - Newcastle

University, Newcastle Upon Tyne, United Kingdom)

email: j.musselle-sexton2@newcastle.ac.uk

Spin crossover is a phenomenon in which a metal ion undergoes a spin transition due to external stimuli such as temperature, pressure, photo-irradiation or electric currents.1 [Fe(Phen)₂(NCS)₂] (Phen =1,10 phenanthroline) is one of the archetype spin crossover systems which has been analysed by various methods including X-ray Diffraction (XRD) with known experimental values for transitions.² Being able to measure the changes in bond length to determine the spin state of the metal ion allows us to set a standard to work by. Light induced excited spin state trapping (LIESST) uses photo-irradiation to cause a spin transition at low temperatures,3 this effect is usually measured by Mossbauer spectroscopy showing the ratio of high spin and low spin atoms in a sample based on magnetic susceptibility. XRD allows us to see the changes in bond length which can be used to determine roughly the spin state, to do this with photo-irradiation means a system has to be designed to allow us to illuminate the sample in the hutch.

Adaptation of this system allows for new spin crossover systems to be found and synthesised, to improve on current research and current properties of these systems.

The applications of these systems including high density memory and display devices, these can only be achieved with spin crossover properties being at relatively easy to obtain conditions. These include being close to room temperature and standard pressure for practical applications to be possible. The presented material will include the development and production of a new light irradiation source that can be mounted within the enclosure of a 3-circle diffractometer and the results of this equipment being used during the collection of data for a novel spin crossover system

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Keywords: Spin Crossover, 3D printing,

MS36-P31

A Systematic study of radiation damage in transition metal chloride complexes with 1,5-cyclooctadiene ligands using diffraction and spectroscopy.

Claire Murray¹, Alex Ganose², Anna Regoutz³, David Scanlon², Amber Thompson⁴

- 1. Diamond Light Source, Didcot, United Kingdom
- 2. Chemistry, University College London, London, United Kingdom
- 3. Materials, Imperial College London, London, United Kingdom
- 4. Chemistry, University of Oxford, Oxford, United Kingdom

email: claire.murray@diamond.ac.uk

Transition metal chloride complexes with 1,5-cyclooctadiene ligands have a variety of applications as catalysts or precatalysts in e.g. hydrogenation and hydrogen-transfer reactions.(1) However, their interactions with X-rays has, to date, been assumed to be non-destructive with no reports in the literature of behaviours indicating radiation damage such as intensity loss in diffraction peaks or peak broadening. Interaction of X-rays with the crystal lattice is an effect that causes well-known problems in biological systems,(2) but this effect is only formally starting to be recognised in chemical crystallography. A survey of the effects of radiation damage to small molecule single crystals(3) demonstrated a relationship between the damage and the intensity of the source. The improving intensity of sources both at central facilities and for in-house instruments is increasing awareness of radiation damage, with a particular lack of understanding for small molecule crystallographers and spectroscopists currently complicating data collection. A series of compounds have been studied where M = Ir, Rh and Cu to, quite literally, shed light on the chemical changes resulting from X-ray exposure via structural and electronic insights. The combination of powder X-ray diffraction, single crystal X-ray diffraction, computational studies and X-ray photoemission spectroscopy reveal the impact of X-ray radiation on these materials in great detail and also provide insight into the importance of identifying appropriate data collection techniques for experiments.

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Keywords: X-rays, Catalysts, Synchrotron

Reversible single-crystal to singlecrystal phase transition of one Zn(II) salicyaldimine complex under non-ambient conditions

Jey-Jau Lee1, Jing-Yun Wu2, Ching-Yun Chang2, Chi-Jou Tsa2

- National Synchrotron Radiation Research Center, Hsinchu, Taiwan
 Department of Applied Chemistry, National Chi Nan University,
- Nantou, Taiwan

email: jjlee@nsrrc.org.tw

One fluorescent Zn(II)–salicyaldimine coordination polymer, [Zn(L^{salyya})(H2O)]n (1; H2L^{salyya} = 4-hydroxy-3-(((pyridin-2-yl)methylimino)methyl)benzoic acid), showing a one-dimensional (1D) zigzag chain structure has been hydro(solvo)thermally synthesized. Kind of different Phase transition structures can be seen as different external perturbations gave to complex 1. High temperature X-ray powder diffraction (XRPD) experiment clearly indicate that the structure of 1 is quite flexible as a result of a reversible 1D-2D single-crystal to single-crystal (SCSC) transformation.

Structure determination on the high temperature X-ray powder diffraction (XRPD) pattern (SDPD) confirmed the removal and rebinding of coordination water molecules of 1 by thermal dehydration gives rise to the dehydration product $[Zn(L^{subyca})]_n$ (1'), which has a dizinc-based two-dimensional (2D) grid-like (4,4)-layer structure and accompanies with changes in coordination sphere and network dimensionality.

In addition to thermal effect on complex 1, external perturbations of pressure and low temperature also make the complex showed phase transition behavior. Detail structural information will show in the presentation.



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Keywords: Zn(II)-salicyaldimine complex , single-crystal to single-crystal, phase transition,

MS36-P33

Crystal nickel(II) complexes with a bidentate hydrazone ligand

Ezequiel M. Vázquez-López¹, Saray Argibay-Otero¹, Olaya Gómez-Paz¹, María Vázquez-Toirán¹

 Departamento de Química Inorgánica, Instituto de Investigación Sanitaria Galicia Sur (IISGS)- Universidade de Vigo, Vigo, Spain)

email: ezequiel@uvigo.es

The Schiff base ligands are frequently used in the synthesis of new coordination compounds with interesting structures and promising properties in different fields. In this work we describe the results of a crystal study about the reactivity in ethanol between nickel(II) acetate and the bidentate Schiff ligand (E)-N'-(4-Hydroxybenzylidene)-4- hydroxybenzohydrazide (H2L). [1]

As is shown in the image, two types of crystal nickel compounds have been isolated. So first crystallized the green octahedral complex [Ni(H2L)2(H2O)2]Ac2·2EtOH and later orange crystals of the square-planar compound [Ni(HL)2]·2H2O were formed after the monodeprotonation of the ligand.

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Keywords: hydrazone, nickel(II), complexes

Evidencing size-dependent cooperative effects on spin cross-over nanoparticles of Hofmann-type [Fe(pz)Pt(CN)₄] coordination polymers.

Laure Guenee¹, Teresa Delgado², Cristian Enachescu³, Antoine Tissot⁴, Andreas Hauser², Céline Besnard⁵

- 1. University of Geneva, Geneva, Switzerland
- Department of physical chemistry, University of Geneva, Geneva, Switzerland
- 3. Department of physics, University of Alexandre Ioan Cuza, Lasi, Romania
- 4. Institut des matériaux poreux de Paris, ENS, Paris, France
- Laboratory of crystallography, university of Geneva, Geneva, Switzerland

email: laure.guenee@unige.ch

Photo-induced processes are of paradigmatic importance in many fields, ranging from biology where light harvesting is the basic process of photosynthesis, to solid-state physics where light can be applied to control the electronic properties of solids. In this context, spin crossover compounds are fascinating photoswitchable materials, with possible applications in sensing or memory devices. However, such materials need to be synthesized as nanoparticles or thin films in order to be incorporated into functional devices. Therefore, the effect of size reduction on the thermo- and photo-switching properties has been abundantly described and modelled within the past few years [1]. However, no direct experimental evidence was made so far on the microscopic origin of the size reduction effects.

Following a previous structural study of the high spin à low spin relaxation dynamics of the porous coordination network $[Fe(pz)Pt(CN)_4] \cdot 2.6 H_2O$ in the bulk state [2], nanoparticles of $[Fe(pz)Pt(CN)_4]$ were synthesised and the HSàLS relaxation through the light-induced excited spin-state trapping (LIESST) effect is investigated using synchrotron X-ray powder diffraction.

We evidence a clear limiting particle size below which the HSà LS relaxation adopts a different mechanism, indicating a drastic change in cooperative processes. We also provide a qualitative explanation of this observed change in cooperativity upon size reduction within the framework of a mechanoelastical model.



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MS36-P35

Crystal structures and bioactivity studies of four novel chalcone and flavonol copper(II) complexes containing Schiff base co-ligand

Aleksandar Višnjevac¹, Adnan Zahirović², Irnesa Osmanković², Emir Turkušić², Emira Kahrović²

- 1. Zavod za fizičku kemiju, Institut Ruđer Bošković, Zagreb, Croatia
- Department of Chemistry, Faculty of Science, University of Sarajevo, Sarajevo, Bosnia & Herzegovina

email: aleksandar.visnjevac@irb.hr

Four new heteroleptic copper(II) complexes having chalcone or flavonol ligands and Schiff base (N-phenyl-5-chlorosalicylideneimine) as co-ligand were prepared, chemically and structurally characterized and investigated as functional biomimetic catecholase models. The complexes were prepared by the solution synthesis and crystal and molecular structures were determined by X-ray diffraction. Complexes were chemically characterized by elemental analysis, infrared and electron spectroscopy as well as by electrochemical measurements. Copper(II) chalcone complexes, with square-pyramidal CuO₄N core, are binuclear, featuring phenolate oxygen from the Schiff base as a bridging ligand, while copper (II) flavonol complexes are mononuclear, and reveal a square planar CuO₃N coordination core. Catalytic activity of the complexes in 3.5-di-tert-butylcatechol oxidation was confirmed by spectrophotometric and electrochemical measurements. Kinetic measurements revealed that the binuclear (chalcone-containing) complexes have enhanced catalytic activity as compared to the mononuclear Cu(II) flavonol complexes. Relatively high k_{cat} values (300 – 750 h⁻¹) confirmed their respectable biomimetic catecholase-like activity.



Keywords: copper, Schiff base, chalcone, flavonol, catecholase activity

MS37- Mechanochemistry: structure and reaction

Chairs: Dr. Hamish Yeung, Dr. Tomislav Friscic

MS37-P01

Photoinitiated solid-state [2+2] cycloaddition reaction in [Zn₂(H₂O)₂(2-Amal)₂(bpe)] (2-Amal = 2-Allylmalonate) crystal

Alexander Volodin¹, Alexander Korlyukov¹, Anna Vologzhanina¹, Ekaterina Zorina-Tikhonova², Aleksandr Chistyakov², Aleksei Sidorov², Igor Eremenko¹-²

- 1. A.N. Nesmeyanov Institute of Organoelement Compounds of RAS, Moscow, Russia
- Kurnakov Institute of General and Inorganic Chemistry of RAS, Moscow, Russia

email: alex.d.volodin@gmail.com

Recently some of us demonstrated that a number of zinc(II) malonates containing 1,2-bis(pyridin-4-yl)ethylene undergo a photoinitiated [2+2] cycloaddition reaction in a single-crystal-to-single-crystal manner [1]. Here, we present the results of our study of a novel photo-sensitive zinc(II) coordination complex containing two unsaturated fragments, namely, 1,2-bis(pyridin-4-yl)ethylene (bpe) and 2-allylmalonate (2-Amal). This complex was obtained from aqueous solution of zinc(II) acetate, 2-allylmalonic acid (H₂Amal) and 1,2-bis(pyridin-4-yl)ethylene (bpe). Ethylene fragments of 2-allylmalonate and bpe are in the reactive positions (Figure, top). At irradiation for 8 hours the complex underwent [2+2] cycloaddition in a single-crystal-to-single-crystal manner to form a 2-((2,3-di(pyridin-4-yl)cyclobutyl)methyl)malonate (Figure, bottom). As both compounds are 3D coordination polymers, the process is the 3D \rightarrow 3D reaction. The conversion rate was 50% in respect to 2-Amal. Further irradiation was accompanied by destruction of the single crystal and formation of an insoluble reaction product.

Figure. Fragment of molecular packing of $[Zn_2(H_2O)_2(2-Amal)_2(bpe)]$ (top), and its photoreaction product (bottom).

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Keywords: solid-state reaction, [2+2] cycloaddition, photoinitiated reaction

MS37-P02

(Mechano)synthesis, structure characterization and pharmacological evaluation of harmine derivatives as new anticancer compounds

Laurie Bodart¹, Sébastien Marx¹, Céline Meinguet¹, Nikolay Tumanov¹, Johan Wouters¹

 Namur Medicine & Drug Innovation Center (NAMEDIC-NARILIS), Laboratoire de Chimie Biologique Structurale (CBS), University of Namur, Namur, Belgium

email: laurie.bodart@unamur.be

Harmine is a natural β -carboline compound, which can be isolated from *Peganum Harmala*, presenting antiproliferative activity. Trisubstituted harmine derivatives were shown to be more potent than mono- and di-substituted ones [1, 2]. Here, new trisubstituted harmine derivatives were designed and synthetized in our group with the aim to overcome the intrinsic resistance of cancer cells to apoptotic stimuli.

The last step of synthesis is performed by mechanosynthesis and compounds involved in this synthesis are characterized by single-crystal X-ray diffraction. However, trisubstituted harmine derivatives often present a moderate solubility at pH 7.4. In this context cyclodextrin complexes were already prepared in our group to improve compounds solubility [2]. Here we propose a new approach to reach this objective. Indeed, the third substituent chosen to be placed on the harmine core contains a pyridine moiety in order to improve compound solubility in comparison with benzyl moiety. Moreover, pyridine increases the tendency towards cocrystal/salt formation. This is also considered as a potential method to modulate the solubility of the compound [3]. The aim of this work is to obtain novel druggable harminebased molecules combining antiproliferative activity in micromolar to submicromolar range and a high solubility at physiological pH in order to allow intravenous injection of these compounds.

L.B. thanks the *Fonds National pour la Recherche Scientifique-FNRS* for her grant and the PC2 technological platform of UNamur.

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Keywords: Harmine, mechanosynthesis, crystal engineering

MS37-P03

Study of thermo- and photochromic behaviour of a hydrazone system obtained by mechanosynthesis

Mégane Van Gysel
1-², Andrea Carletta ${}^{\rm i},$ Nikolay Tumanov
¹, Johan Wouters ${}^{\rm i}$

- Namur Medicine & Drug Innovation Center (NAMEDIC-NARILIS), Laboratoire de Chimie Biologique Structurale (CBS), University of Namur, Namur, Belgium
- Namur Institute of Structured Matter (NISM), Laboratoire de Chimie Biologique Structurale (CBS), University of Namur, Namur, Belgium

email: megane.vangysel@unamur.be

Hydrazones are compounds widely studied. They can be made by several synthetic pathways, such as a condensation reaction between a hydrazine or hydrazide with a ketone or aldehyde [1]. These molecules are constituted by an azomethine group, characterized by the fragment C=N-N, allowing the use of hydrazones in various fields of chemistry. These molecules have many potential applications: they are used in dyes and in conductive materials to name a few [1]. In pharmaceutical field, several hydrazone-based prodrugs of isoniazid have shown less undesired side effects when compared with isoniazid [2]. These molecules can also be studied for their potential thermo- and photochromic properties.

Thermo- and photochromism are color change phenomena induced by temperature variation and absorption of electromagnetic radiations, respectively. These phenomena have many applications: information storage, optical switching devices (optical glasses), etc. [3].

In this work, we are interested in a hydrazone system obtained by a condensation reaction between isoniazid and *o*-vanillin. This molecule is cocrystallized with various cocrystal formers with the aim to modulate its photo- and thermochromism [3]. Both syntheses of the chromophore and of its cocrystals are accomplished by mechanosynthesis. All obtained solid forms are characterized by powder X-ray diffraction and single-crystal X-ray diffraction. Photochromism is studied by UV-Vis diffuse reflectance.

Authors acknowledge ARC (UNamur – UCL) for financial support.

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Keywords: mechanosynthesis, cocrystals, hydrazones

MS38- X-Ray diffraction on the micro-s and ps time scale

Chairs: Dr. Gergely Katona, Dr. Ullrich Pietsch

MS38-P01

Current status of time-resolved X-ray crystallography beamline TPS 09A at Taiwan photon source

Hwo-Shuenn Sheu¹, Yi-Wei Tsai¹, Ying-Yi Chang¹, Wei-Rein Liu¹, Yin-Yu Lee¹, Lai-Chin Wu¹, Chung-Kai Chang¹, Kuan-Li Yu¹, Shih-Lin Chang²

National Synchrotron Radiation Research Center, Hsinchu, Taiwan
 Department of Phylics, National Tsing Hua University, Hsinchu, Taiwan

email: hsheu@nsrrc.org.tw

The TPS 09A beamline of Taiwan Photon Source (TPS) is designed for time-resolved laser pump X-ray probe crystallography experiments. TPS 09A has opened to general X-ray scattering users since September 2016. TPS is a third generation synchrotron source which operate at 3.0 GeV, 400 mA (design gold 500 mA), with beam emittance of 1.6 nm rad. The source of TPS 09A beamline is delivered from two IU22 undulators which provide temporal coherence X-rays of 5.6-25 keV. Follow the double crystal monochrotromator (DCM with two Si(1 1 1) crystals) is a horizontal focusing mirror. The beam size at the entry of experimental hutch is about 700 mm x 600 mm (H x V). Inside the hutch, the X-ray focus by a compound reflection lens, a Juelich chopper (the chopper will be delivered in the summer of 2019) and a Huber 9-circles diffractometer. Server detectors can be choiced for X-ray scattering, such as Pilatus 200K, Perkin Elmer XRD 1611 xP, and CsI point detector. A new area detector is now planning. A Ti-Sapphire with 35 fs pulse laser is located at the second hutch and can bring the 800 nm or 400 nm pulse laser to sample position. The synchrotron X-ray bunch length is about 35 ps. For lack of the Juelich chopper, we have test a las er pump X-ray probe time resolve X-ray diffraction experiment by using single bunch injection at TPS. The electron current is maintained at about 2 mA with top up injection for every 8 mins. The diffraction intensity and position of Si (111) is monitored during different laser pumping time. The FWHM of the intensity variation is about 250 ps. It demonstrated that the time scale of laser pump X-ray probe can be determined in 100 ps time scale. The structure of the excited sates of some organic and inorganic luminesce compounds are under investigations.



Keywords: Time-resolved X-ray Crystallography, Laser Pump X-ray Probe, Synchrotron Radiation

MS38-P02

Sub-na and sub-ps time resolved diffraction at cristal beamline - SOLEIL synchrotron

Sylvain Ravy¹, Claire Laulhé², Alessandra Ciavardini², Amélie Jarnac², Fabien Legrand², Erik Elkaim², Felisa Berenguer², Pierre Fertey²

1. Laboratoire de Physique de Solides, Orsay, France 2. Synchrotron-SOLEIL, Gif-sur-Yvette, France

email: sylvain.ravy@u-psud.fr

The study of out-of-equilibrium dynamics in crystalline solids has become an important topic of modern condensed matter physics. Out-of-equilibrium states are obtained by irradiation with ultra-short laser pulses in the optical range, which induces electronic transitions on a timescale at which the lattice is considered to be frozen. Such photo-induced dynamics are studied experimentally in the socalled 'pump-probe' scheme, in which the sample is excited (pumped) by a fs optical laser pulse and probed by a pulse of an eventually different wavelength such as X-rays. Pulsed hard X-ray absorption to study photo-induced transitions in condensed matter under non-equilibrium conditions, and thus uniquely give access to precise information on the dynamics of atomic structures at the Å-scale.

In laser pump - X-ray probe experiments, the time resolution is in practice limited by the X-ray pulse duration. SOLEIL synchrotron, in its standard mode of operation, provides pulses of typically 80 ps FWHM [1]. X-ray pulses as short as 10 ps and 100 fs are also produced, in the "low- α " mode of operation [2] and with the femto-slicing source [3], respectively.

The undulator-based diffraction beamline CRISTAL enables studies of ultrafast structural dynamics using those short X-ray pulses. The sample is excited by 800 nm, 25 fs FWHM laser pulses provided by a regenerative Ti:Sa amplifier (max. output power 6 mJ @ 1 kHz). The subsequent changes in the sample's atomic structure are studied in the time domain Dt, by measuring its diffraction out of a monochromatic incident beam. The X-ray flux available at sample, which depends on the aimed time resolution, ranges from 6.108 ph/s for 7 keV, 70 ps FWHM X-ray pulses at a repetition rate of 1 kHz, to 1.106 ph/s for 7 keV, 100 fs FWHM X-ray pulses at the repetition rate 1 kHz. A 2D, gateable detector is used to collect the scattered intensities, which gives access to a large portion of reciprocal space for each single measurement. Various sample environnements have been made available, including a near-ambient temperature Peltier cell, a 5 K cryostat, and a 30 K N₂/He blower.

The poster will present the instrumentation developped at CRISTAL beamline for pump-probe diffraction experiments, as well as recent exemples of measured ultrafast structural dynamics.

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Keywords: Diffraction, synchrotron, time-resolved

MS38-P03

Understanding elastically driven cooperativity in molecular photomagnetic materials

Alix Volte¹, Céline Mariette¹, Marie-Laure Boillot², Marco Cammarata¹, Giovanni Azzolina¹, Matteo Levantino³, Roman Bertoni¹, Maciej Lorenc¹

- 1. Institut de Physique de Rennes, UMR 6251, Rennes, France
- Institut de Chimie Moléculaire et des Matériaux d'Orsay, Orsay, France
- 3. ESRF, Grenoble, France

email: alix.volte@univ-rennes1.fr

Materials can be controlled via physical parameters like pressure or temperature. With the advent of ultrashort lasers pulses (typically femtosecond), light excitation has been added to the panel of available techniques for materials control. Two of the major aspects in so-called photo-induced phase transitions are:

- reversibility, meaning the ability to switch back and forth between two states,
- efficiency, corresponding to the ratio of the amount of transformed material on the quantity of provided light.

One possible approach to amplify the photoresponse is based on the material elastic properties. This was demonstrated for a light-sensitive and volume-changing Spin Crossover (SCO) material [1], meaning, a molecular crystal in which the unit cell is built with SCO molecule(s). In this molecule, the ligand field result in a splitting of the 3d levels of the metal ion (FeIII) into low energy and high energy ones. The population of high energy levels (at high temperature) changes the spin state and is accompanied by strong changes in Fe-ligand distances (and thus unit cell volume).

The sudden generation (via a laser pulse) of a high enough fraction of photo-excited molecules (switched from Low spin to High spin state) creates local negative pressure. This drives lattice expansion that can induce additional switching of neighboring molecules through positive feedback effect. This cooperative effect is associated as expected with a well-defined threshold mechanism. We can actually see (insert in Fig.) that the fraction of transformed molecules after photoexcitation decreases monotonically for low excitation fraction, while it increases non-linearly in the nanosecond time scale for higher ones.

To unambiguously discriminate between spin state conversion and structural changes, we performed Xray time-resolved diffraction study at synchrotron ESRF. The diffraction patterns measured from ps to µs time delays on nanocrystals powder films give a direct signature of the ultrafast volume expansion. Quantitative analysis (Rietveld) of the powder spectra at ps time scale allows going deeper into the understanding of the cooperative aspects of the photo-induced spin conversion in these molecular materials.

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Keywords: x-ray powder diffraction, photo-induced transitions, time-resolved transitions

MS38-P04

Multscale real-time XRD probing of the semiconductor to metal ultrafast phase transition in Ti_3O_5 nanocrystals

Céline Mariette¹, Alix Volte¹, Hiroko Tokoro², Shin-Ichi Okhoshi², Henrik Lemke³, Matteo Levantino⁴, Marco Cammarata¹, Maciej Lorenc¹

- 1. Institut de Physique de Rennes Université de Rennes CNRS, Rennes, France
- Department of Chemistry, School of Science, The University of Tokyo, Tokyo, Japan
- 3. Paul Scherrer Institute, Swissfel, Bernina, Villingen, Switzerland
- 4. ESRF, Grenoble, France

email: celine.mariette@univ-rennes1.fr

Last decades have seen tremendous technical progress in the development of pulsed Xray sources. Synchrotron sources can now produce 100ps duration pulses with enough photons to allow quantitative analysis. The emergence of free electron laser brought the pulse duration a step shorter, typically 10fs, and even more bright. This leads to the ability to probe electrons and atoms on the time scale of their respective motions, opening a completely new field of investigation to physicians and material scientists: the science of out-of-equilibrium processes.

Since the 2000s and the pioneering time resolved XRD experiments, we can now "see" atomic motions in real time on fs time scales. Today's challenge is not only to see but also to be able to "act" on matter in an ultra-fast and controlled manner. This means inducing an ultrafast permanent change, ultimately reversible, in a material. This requires a deep understanding of the ultrafast structural dynamics but also the propagation process of the induced deformation on longer time and space scales. It was recently demonstrated experimentally and theoretically a self-amplified responsiveness in a spin-crossover material [1] during its delayed volume expansion.

Time-resolved XRD is a direct probe of volume changes and structural rearrangement in materials.

Such experiments are still highly challenging. However we will show how that the implementation of quantitative structural analysis (rietvelt refinement) can be extended to these out-of-equilibrium studies. Our talk will focus on Titanium Pentaoxide (Ti3O5), a protype of multistability which undergoes phase transitions between different forms (so called α , β , λ), that can be monitored by temperature, pressure, electric field and laser pulses. The stability of the phases is strongly related to the size of the crystallites. In particular λ phase is more stable in nanocrystals thus making the system bi-stable at ambient temperature with obvious interest for pure as well as applied science[2] (fig. 1). We will present the study of this ultrafast phase transition in Ti3o5 nanocrystals, for which we performed three major experiments:

- Time resolved powder XRD on ps time-scale (Swissfel, Bernina)[3]
- Multiscale (from 100ps to millisecond) time resolved XRD (beamline ID9, ESRF).
- Multiscale optical spectroscopy pump/probe measurements (IPR, rennes).

We will show how this combined approach gives us new insight into this reversible semi-conductor to metal ultrafast phase transition

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Keywords: phase transition, ultrafast XRD

MS38-P05

High resolution guinier powder diffractometer combined with multilayer optics

Stefan Griessl¹, Maximilian Reh¹, Thomas Holz², Reiner Dietsch², Norman Huber¹

1.HUBER Diffraction, Rimsting, Germany 2. AXO Dresden GmbH, Dresden, Germany

email: ecm31@nion.de

The Huber double radius Guinier camera G670 is characterized by its short measurement time and high-resolution diffractograms. In addition to the successfully working Johansson monochromators curved multilayer optics from AXO DRESDEN were tested. Measurements were carried out with Cu Ka, Mo Ka, and Ag Ka radiation (8.0 keV, 17.4 keV, 22.1 keV). Thus, a direct comparison between Johansson monochromators and multilayer optics was possible in terms of signal-to-noise ratio, full-width at half maximum (FWHM) of the diffraction peaks and the quality criterion of Jenkins and Schreiner. Various substances were tested both as powder on a flat sample and in a capillary. The capillary measurements showed very high intensities, especially with the multilayer optics. The wavelengths of the X-radiation used, together with the excellent resolution, make pair distribution function analyses feasible. Hence, the used instrument enables fast and precise determination of all important parameters of a powder sample.

MS39- The use of x-rays and neutrons for experiments in nanoscience

Chairs: Dr. Rainer Timm, Prof. Jordi Arbio

MS39-P01

Multiple Bragg reflections of neutrons related to a strong allowed reflection Si(004) in a cylidrically bent perfect crystal

Pavol Mikula1, Jan Šaroun1, Miroslav Vrána1, Vyachelav Em2

- 1. Neutron Physics Department of Nuclear Physics Institute ASCR, v.v.i., Řež near Prague, Czech Republic
- 2. National Research Centre 'Kurchatov Institute', Moscow, Russia

email: mikula@ujf.cas.cz

The experimental results of particular studies of multiple Bragg reflection (MBR) effects related to a strong Si(400) reflection in the cylindrically bent perfect crystal at the neutron wavelength of 0.162 nm are presented. It has been found that the MBR effects strongly depend on the diffraction geometry of the Si(004) planes with respect to the cut of Si slabs. Contrary to a common view that the MBR effects could be considered negligible or represent maximally a few percent of an effect related to a single allowed reflection, it has been found that in the case of a particular diffraction geometry their reflecting power can be comparable even much higher than the primary Si(004) reflection. For searching of the MBR effects, the azimuth-Bragg angle relationship for the 004 primary reflection in the diamond structure as displayed in the attached figure, was used. The horizontal dashed line corresponds to the Si(004) reflection for $\lambda = 0.162$ nm.



Keywords: Neutron diffraction, bent perfect crystal, multiple reflection

MS39-P02

Inside source x-ray fluorescent holography on NiO

Gyula Faigel¹, Gábor Bortel¹, Miklós Tegze¹, Borislav Angelov²

1. Wigner Research Centre for Physics, Budapest, Hungary

2. ELI Beamlines Project Division, Dolní Břežany, Czech Republic

email: gf@szfki.hu

Atomic resolution x-ray holography can be realized by using the atoms of the sample as inside sources [1,2] or as inside detectors [3]. However, until now there were only very few experiments in which the atoms played the role of inside sources. The reason is twofold: (i) technically, inside detector experiments are much easier; (ii) using atoms as inside detectors one can measure holograms at many energies on the same sample, which helps the reconstruction process. In this work we show that using new technical developments, inside source holograms can be taken much faster (within 1 second at a synchrotron source) than inside detector holograms and applying a sophisticated evaluation method high quality reconstruction from a single energy hologram can also be obtained. The adaptation of this technique to XFEL-s opens a series of new possibilities in structural studies. For example, one can obtain 3D structural information of very short lived transient structures, appearing in highly non-ambient conditions: high pressure, high magnetic fields, high temperatures, where experimental conditions cannot be repeated with exact control.

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Keywords: x-ray holography, atomic resolution

MS39-P03

Local structure observation of Sm doped RB_6 (R: rare earth)by white neutron atomic resolution holography

Shoichi Uechi¹, Yuki Kanazawa¹, Youhei Fukumoto¹, Kenji Ohoyama¹, Maximilian Lederer², Naohisha Happo³, Kouichi Hayashi⁴, Wataru Matsuura⁵, Humitoshi Iga⁵

- 1. Ibaraki University, Tokai, Japan
- 2. Friedrich Alexander University, Erlangen, Germany
- 3. Hiroshima City University, Hiroshima, Japan
- 4. Nagoya Institute of Technology, Nagoya, Japan
- 5. Ibaraki University, Mito, Japan

email: 18nm907f@vc.ibaraki.ac.jp

Physical properties of materials are often controlled by impurity doping. Thus, understanding the local structures such as distorted structures around the dopant is important to clarify origins of the properties. However, such local structures cannot be observed by diffraction because there is no translational symmetry.

Recentry, atomic resolution holography using x-rays and photoelectrons has been depeloped, which can observe local structures around dopants in the range of 20 Å of three-dimensional area. Thus, atomic resolution holography is the best probe to investigate local structures.

On the other hand, it is difficult to observe light elements such as H, B or O by x-rays and photoelectrons. Therefore, we have developed atomic resolution holography using white neutrons, which are sensitive to light elements, at Japan-Proton Accelerator Research Complex at Tokai Japan [1]. We have already succeeded in visualising local atomic structure in B doped Si, which is the most important semiconductor, and Eu 1% doped CaF₂, which is a typhical scintilation crystal. For CaF₂, we found that there exist excess F around doped Eu [1]. Based on this success, we are trying to apply this novel technique to various fields of materials science.

In this study, we focus on a strongly correlated electron system RB₆ (R: rare earth). When Sm is doped in LaB6 and YbB6, it behaves as Sm2+ in the former and as Sm3+ in the latter [2]. We expect that the difference of local structures around Sm may play a role in this change of valency. White neutron holography experiments were performed on a single crystal La¹¹B₆ and Yb¹¹B₆ with 2% doped Sm. We succeeded in reconstruction of the local structure of R around Sm using data in the neutron energy range from 10 meV to 200 meV. We confirmed that R around the Sm dopant are located at the same positions as in pure RB₆, meaning that Sm doping does not effect R structure. Moreover, we also succeeded in reconstruction local structure of 11B viewed from Sm. These results indicate that neutron atomic resolution holography is an effective probe for investigations of local structures even for various materials which include light elements.

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 J.M. Trascon, et al., (1980) J. Physique, 41, 1135.

Keywords: Neutron, Local structure, Holography

MS39-P04

Enhancement of accuracy of neutron atomic resolution holography

Kanazawa¹, Youhei Fukumoto¹, Shiyouichi Uechi¹, Kenji Ohoyama¹, Maximilian Lederer², Naohisa Happo³, Koichi Hayashi⁴, Masahide Harada⁶, Kazuo Tsutsui⁶

- 1. Ibaraki University, Tokai, Ibaraki, Japan
- 2. Friedrich-Alexander University, Erlangen, Germany
- 3. Hiroshima City University, Hiroshima, Japan
- 4. Nagoya Institute of Technology, Nagoya, Japan
- 5. Japan Atomic Energy Agency, Tokai, Ibaraki, Japan
- 6. Tokyo Institute of Technology, Yokohama, Japan

email: xxx.ypuuurikin6@docomo.ne.jp

Needless to say, the properties of the materials strongly depend on arrangements of atoms. In particular, for functional materials, the properties are controlled by doping a small amount of foreign elements, in which slight difference between the local atomic structures around the dopants and average structures of the crystals is important for the properties. However, the diffraction cannot observe such local structures because of lack of translational symmetry. Atomic resolution holography (ARH) is the unique technique that can directly observe the local structures in a three dimensional space within 20 Å from the selected atoms (dopants). On the other hand, ARH reproduces artifacts in principle, so called twin images. Note that such artifacts can be avoided by using data obtained with many different wavelengths [1]. Thus, we are developing ARH using pulsed neutrons at Japan Proton Accelerator Research Complex at Tokai, Japan, which can obtain holograms of 130 different wavelengths at once by the time of flight method [2].

We measured a single crystal of 0.13 at% B doped Si, and succeeded in visualizing the local structure around B; we confirmed that most of doped B are located at the substitutional site. As a next step, to estimate positional accuracy of obtained atomic images of B doped Si quantitively, we measured a single crystal of NaCl as a standard sample. For neutron ARH, prompt γ -rays from the dopants are observed. Thus, as a required condition of good standard samples, the elements in the samples have to generate high intensity prompt y-rays. Though intensity of y-rays from Na and Cl is about 500 times smaller than that of B, total No. of Na and Cl atom is 300 times larger than that of the doped B in Si; therefore, ARH of NaCl single crystal is feasible. Besides, NaCl is a good example to confirm whether materials with elements which generate weak prompt γ -rays can be targets of neutron ARH. In our presentation, the results of B doped Si and the estimation of accuracy based on the analysis of NaCl will be reported.

From the recent results, we believe that neutron ARH is a powerful probe for determination of local structures around dopants in various and exotic materials. In particular, investigations of hydrides will be feasible in near future.

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Keywords: neutron, local structure,B doped Si

MS39-P05

Use of X - ray diffraction method for residual stresses measurements in lean duplex stainless steel welds

Naima Ouali1, Brahim Belkessa2, Billel Cheniti2, Walid Bedjaoui2

1. Metallurgy and mechanical departement, Algiers, Algeria 2. CRTI, Algiers, Algeria

email: oualinaima@yahoo.fr

In welding processes, the used of adequate energy is very important, it should be sufficient to prevent sticking but not too large to prevent grain growth, resulting in intense residual stresses and a decrease in mechanical properties of materials [1]. This research investigated effects of weld heat input and thus the cooling rate on mechanical properties in particularly residual stresses evolution.

The studied material was received in the form of 6mm lean duplex stainless steel rolled sheet, LDX 2101(EN 1.4162, UNS S32101). The plates with single-V groove were joined using a TIG process for three different heat inputs.

Microstructures of different zones were observed and captured using optical microscope and scanning electron microscope (SEM) with an EDS analyzer. The ferrite contenwas assessed in light optical microscope using image analysis software. The X-ray diffraction method which employs Bragg's theory was used to evaluate the residual strains then the residual stresses present within the weld. The extents of longitudinal and transverse residual stresses were carried out on the basis of the $\sin^2 \psi$ method, which is very employed for polycrystalline materials [2].

The microstructural analysis revealed different regions with a fusion zone which contains more austenite than the heat affected zone HAZ and parent material [3]. It is observed an increase in amount of austenite in weld metal within heat input increases, this low ferrite content in the weld can be attributed to high Ni content in the filler metal (7.5-9.5 % Ni)and the presence of austenite stabilizer N₂ in shielding gas.

The measurements of RS were made on the $\{211\}$ atomic plane of the studied material at 2θ = 156.105°, presented compressive stresses in longitudinal and transverse directions reaching a maximum stresses in the weld area. These residual stresses are due to high plastic deformation and temperature gradient involved in weld metal.

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Keywords: Lean duplex stainless steel, XRD method, residual stresses

MS40- Crystallization for small and large molecules

Chairs: Prof. Bernhard Spingler, Prof. Terese Bergfors

MS40-P01

The co-crystallization of the DNA sequences – 5'-CGTGAATTCACG-3'(S1) and 5'-CGCGAATTCGCG-3'(S2) with fluorescent markers and ligands

Hristina Sbirkova-Dimitrova¹, Rosica Nikolova¹, Louiza Dimowa¹, Rusi Rusev¹, Boris Shivachev¹

 Institute of Mineralogy and Crystallography "Acad. Ivan Kostov", Bulgarian Academy of Sciences, Acad. G. Bonchev str., bl. 107, Sofia, Bulgaria

email: sbirkova@mail.bg

With the DNA sequences such as 5'-CGTGAAT-TCACG-3'(S1) and 5'-CGCGAATTCGCG-3'(S2), for which are characteristic regions rich in AATT bases, bind many drug forms for treatment of oncology diseases and marker dyes used in fluorescence microscopy. These DNA sequences are also interesting because of the presence of a DNA binding site with the restriction enzyme *EcoRI*. [1]

Our aim is to co-crystalize DNA with DAPI and other fluorescent molecules. The co-crystallization include DAPI, TO, Berenil and some new fluorescent ligands (AK3-4, AK3-9, DL72 and DL89). DAPI and Berenil lie in the narrow minor groove near the center of the B-DNA fragment positioned over the A-T base pairs. They are bound to the DNA by hydrogen interactions. DAPI inserts itself in the minor groove, displacing the ordered spine waters [2]. DAPI, TO and Berenil show strong fluorescence when bound to DNA, which led to the rapid adoption of these stains for fluorescent labeling in fluorescence microscopy [3]. For verification of DNA ligand interaction, was used Fluorescence Intercalation Displacement (FID) method (Figure 1A). Fluorescence spectroscopy is an effective methodology (nM quantities) suitable for checking and pre-analyzing the expected result of the co-crystallization.

The oligonucleotides of S1 and S2 were crystallized by the vapor diffusion method. The crystallization conditions contained cacodylate buffer (pH 6.5-7.5), alcohol (2-propanol or methylpentanediol (MPD)), cations (Mg²⁺, Ba²⁺) and polyamines (Spermine). Finding the right conditions for obtaining good single crystals of the particular DNA sequences has required a lot of careful testing. As found in the process of optimization of the crystallization conditions, for the tested sequences S1 and S2 crystal growth was observed only in the Spermine plates. Dry (lyophilized) oligonucleotide sequences were dissolved in buffer to 2mM concentration. The buffer solution consists of 60 mM NaCaCo (pH 7.0), 17 mM MgCl², 2 mM Spermine. Ligands were dissolved in the same buffer to 2mM concentration. Crystals were grown by the "hanging drop" method and 1.5µl (2 mM) ligand (3 µl total drop volume) was added to 1.5 µl DNA (2mM) at room temperature equilibrated against 50% MPD. Crystallization plates were stored in controlled temperature rooms (16-20°C). Large crystals (0.4 x 0.3 x 0.25 mm³) suitable for single crystal X-ray analysis, crystals formed within a month (Figure 1B).

Figure 1. a) Graphical representation of FID data for the impact of DAPI, Berenil, TO, AK3-4, AK3-9, DL89 and DL72; **b)** Obtained crystals.



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Keywords: DNA, FID, Ligands

MS40-P02

A high-throughput crystallisation facility interacting with the new VMXi beamline at the Diamond Light Source

Halina Mikolajek¹, James Sandy¹, Juan Sanchez-Weatherby¹, Thomas Sorensen¹

1. Diamond Light Source, Didcot, United Kingdom

email: halina.mikolajek@diamond.ac.uk

A new state of the art crystallisation platform for soluble and membrane proteins has been created within the Research Complex at Harwell combining the expertise of Diamond Light Source, MPL and PPUK. This platform is high-throughput and provides users with an easy route into the VMXi beamline, the new fully automated in situ and serial crystallography beamline at the Diamond Light Source, UK. Users from all over the world have access to this facility and can also deliver their samples for crystallisation experiments. Crystallisation can be set up and stored at 4°C as well as at room temperature with humidity control and in lipid cubic phase (LCP) in a number of different plate types. A large number of commercial screens are available and customised screens can be designed and prepared easily. The crystallisation experiments are imaged using Formulatrix Rock Imagers and can be viewed via Rock Maker as well as SynchWeb, which is available on the VMXi beamline. Users can evaluate their crystallisation hits on the VMXi beamline and cycle faster than ever between optimisation cycles to obtain their molecular structure.

Keywords: Crystallisation, Facility, VMXi

MS40-P03

How porous materials improve protein crystallization? Principle of dominant protein-protein adhesion mode

Jindrich Hasek¹, Tereza Skálová¹, Tomáš Kovaĺ¹, Jarmila Dušková¹, Terézia Kovaĺová¹, Leona Švecová¹, Petr Kolenko¹, Jan Dohnálek¹

1. Institute of Biotechnology, Czech Academy of Sciences, Praha, Czech Republic

email: hasekjh@seznam.cz

Initiation of crystallization on heterogeneous objects immersed in crystallization drop is well-known, but not well understood phenomenon. In our previous studies [1,2], we have explained details why selection of dominant adhesion mode is generally very important factor in protein crystallization, no matter the crystallization material and the method used. When applied to the protein crystallization in porous materials, it offers a non-conflict explanation of initiation of the crystal-seeds and microcrystals growth in depressions or pores in the surface of heterogeneous materials. The protein molecules adhered specifically at the pore inlets, have restricted access to the adhesion patches oriented toward heterogeneous surface. Uniformity of the remaining adhesion modes exposed into the solution induces also uniformity of the adhesion modes realized in the protein clusters formed at the pore inlet. Thus, the clusters formed in cavities are more regular and stable than those formed in free solution. When the growing crystal-seed reaches its limit size, it breaks off at the pore inlet (the more disordered segment of crystal) and the well-defined microcrystal releases into solution-

The simplest way for preparation of porous material with the required size and shape of cavities is imprinting objects (e.g. proteins) of the required size and shape into the polymer matrix. Theoretically, the cavities 3-20 times larger than the size of a target protein molecule can produce nanocrystal-seeds with sizes in range 50–500 nm. Narrower distribution of cavity sizes is expected to lead to more uniform distribution of crystal sizes. High density of small cavities on the substrate surface seems to be negative, namely when our intention is to grow single crystals. Chemistry of the heterogeneous material decides about the dominant adhesion mode governing the protein crystal growth and responsible for the resulting crystal form.

Experimental observation of the described processes at the structured surfaces or in nano-pores is not possible. However, because our theory and the former interpretations [3] (based on increased protein concentration in cavities) have different impact on **design of the "protein-crystal-growth initiators"**, the prevailing molecular mechanism can be revealed by experiments with well-defined pore sizes and adhesion quality.

The outlined principle of a single dominant adhesion mode and the protein orientation effect in the confined concave space help in a controlled production of protein crystals, e.g. production of a large number of quality microcrystals for serial crystallography at XFEL sources.

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Keywords: protein crystallization, principle of dominant adhesion mode, porous materials

MS40-P04

Crystallization of the quadruplex (GGGGTTTTGGGG)₂ with BRACO19

Rositsa Nikolova¹, Hristina Sbirkova-Dimitrova¹, Rusi Rusev¹, Louiza Dimova¹, Boris Shivachev¹

1. Institute of Mineralogy and Crystallography, Sofia, Bulgaria

email: rosica.pn@clmc.bas.bg

One of the approaches for to development of new anticancer compounds focuses on the design and screening of compounds, small molecules that interact selectively with cancers cells. As telomeres are G-rich noncoding regions located at the end of chromosomes. The telomere shortens with each cell division. When it reaches a critical length it triggers DNA damage response which leads to cell death. Cancer cells have active telomerase (responsible for the maintenance of telomeres) that maintain a shorten but not critical telomere length, provoking those cells to unlimited cell division. G-rich telomeres are in practice forming G-quadruplex structures in vivo. Ligands that selectively bind and stabilize G-quadruplex, are interfering with telomerase activity: maintenance and elongation of telomere. We report on the interaction of the (GGGGTTTTGGGGG)₂ sequence with the small molecule BRACO-19. In addition, single crystal of the DNA complex with BRACO19 were grown (Figure 1). The initial crystallization conditions included KCl, KCaCO pH7.5, MgCl₂, Spermine and MPD. The crystals were brownish in color and diffracted up to 2.5 Å resolution. In order to solve the crystal structure, currently diffraction limit and crystal quality are optimized through modification of the crystallization conditions.



Figure 1. Observed crystals of (GGGGTTTTGGGG), with BRACO19

References:

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Keywords: G-4, quadruplex, BRACO19

MS40-P05

Crystallization of putative copper binding CrdA protein and helicase-like HP1026 protein from the human pathogen *Helicobacter pylori*

Dubravka Matković-Čalogović¹, Ivana Kekez¹, Vigor Matković¹, Mario Kekez¹, Giuseppe Zanotti²

- 1. Department of Chemistry, Faculty of Science, University of Zagreb, 10000 Zagreb, Croatia
- 2. Department of Biomedical Sciences, University of Padua, Padua, Italy

email: dubravka@chem.pmf.hr

Helicobacter pylori bacteria colonize the human stomach and can cause development of gastric diseases like atrophic gastritis, peptic ulcer, gastric adenocarcinoma and lymphoma of the mucosa-associated lymphoid tissue (MALT).¹ For this purpose, proteins involved in survival of this bacterium have become an important target of research. Among them is the putative cooper binding CrdA protein and helicase-like HP1026 protein which were investigated in this work. CrdA is required for keeping the concentration of free copper ions below toxic levels² while HP1026 has been classified as one of the heat shock proteins that are generally involved in regulation of the urease activity and adhesion to the epithelial cells.³

In order to reveal the structural and functional properties of these proteins, cloning, purification and crystallization trials (performed by the sitting and hanging drop vapor diffusion methods) have been carried out. Since crystallization of CrdA was not successful, the SUMO-fusion-CrdA protein incubacted with Cu2+ ions gave crystals, so far of poor diffraction quality. The optimization of crystallization is in progress. In the case of the HP1026 protein the thermal stability assay was also investigated. ATP-g-S and ADP strongly affected the protein stability by shifting the protein-complex denaturation to higher $t_{\rm m}$ values by D +3.52 °C and +5.18 °C, respectively. This experiment together with the ATP hydrolysis assay (previously performed) was another confirmation that HP1026 belongs to the class of ATPase proteins. The results of this thermofluor assay were also applied in the crystallization experiments and crystallization of HP1026 supplemented with ADP resulted in hexagonal-shaped crystals. Diffraction data of HP1026 were measured at the XRD1 beamline (Elettra, Italy) but only to the resolution of 4 Å. The crystals belong to the hexagonal system (a = 116.22(2) Å, c = 238,38(2) Å, space group P3₁21). Since the sequence similarity of HP1026 and homologues with the known crystal structures is 30% or less, solving of structure of HP1026 was not successful so far. We are working on obtaining better quality crystals.



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Keywords: crystallization, CrdA, HP1026

MS42- New approaches to structure solution by crystallography and CryoEM: computational features and new algorithms

Chairs: Prof. Isabel Usón, Dr. Tom Burnley

MS42-P01

A modeling study for cholesterol binding proteins, NPC family protein

Hyejin Yoon1, EunSook Joo2, Soonmin Jang3, Hyung Ho Lee1

- 1. Department of Chemistry, Seoul National University, Seoul, Korea South
- 2. Faculty of Biotechnology, Jeju National University, Jeju, Korea South
- 3. Department of Chemistry, Sejong University, Seoul, Korea South

email: yoonhj@snu.ac.kr

Understanding of the detailed dietary cholesterol exchange in cellular environment still remains as an open subject. The mutation of one of NPC1 (Niemann-Pick type C1) and NPC2 (Niemann-Pick type C2), which are main players of cholesterol control in lysosome, leads to disease, called Niemann-Pick disease type C (NPC) disease. Meanwhile, the transmembrane protein NPC1L1 (Niemann-Pick type C1 like 1), which is related to the dietary cholesterol absorption process in small intestine, shares sequence homology with NPC1. However, unlike NPC1, NPC2 is not involved in cholesterol internalization with NPC1L1. The structure of NTD of NPC1 in complex with cholesterol (PDB id: 3GKH and 3GKI) was known while only cholesterol free NTD (PDB id: 3QNT) is known for NPC1L1. It is noted that the whole cryo-EM structure of NPC1 is determined (PDB id: 3JD8).

We compared the cholesterol complex of NPC1L1 and NPC1 with molecular docking followed by molecular dynamics study for better understanding of these underlying behavior. The NTD molecular dynamics simulation of NPC1 and NPC1L1 complex with cholesterol shows different structural and dynamical features. The difference in cholesterol internalization mechanism between NPC1 and NPC1L1 must be closely related to these structural and dynamical behaviors. We believe the current study can contribute understanding of cholesterol absorption/re-absorption process via NPC1 and NPC1L1 and their difference with atomic detail.

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 Gong X., et al. "Structural insights into the Niemann-Pick C1 (NPC1)- mediated cholesterol transfer and Ebola infection." Cell, Vol. 165, (2016), pp 1467-1478.

Keywords: Molecular dynamics, NPC protein

MS42-P02

Expanding partial structures by assembling most probable side chain composition

Rafael Borges¹, Massimo Sammito¹, Claudia Millán¹, Nicolas Soler¹, Ana Medin¹, Iracema Caballero¹, Marcos R. M. Fontes², Isabel Usón³

- Department of Structural Biology, Institute of Molecular Biology of Barcelona (IBMB), Spanish National Research Council (CSIC), Barcelona, Spain
- Department of Physics and Biophysics, Biosciences Institute (IBB), São Paulo State University (UNESP), Botucatu, Brazil
- 3. Department of Structural Biology, Catalan Institution for Research and Advanced Studies (ICREA), Barcelona, Spain

email: rjborges@ibb.unesp.br

Knowledge of biological structures and their interaction plays an essential role in the comprehension of biological mechanisms. Crystallography and recently CryoEM provide macromolecular models in atomic detail. CryoEM requires the interpretaion of a map of heterogeneous resolution, while crystallography requires to overcome the bottleneck of phasing. Phasing through multisolution placement of ubiquitous small fragments, such as alpha-helices and beta-strands, with PHASER [1] followed by density modification and tracing with SHELXE is now established as an effective method to solve the phase problem, provided the structure is not too large and data to high resolution are available [2]. When the resolution limit of the diffraction data does not reach 2 Å, and if the helical content is low, fragments may still be correctly placed, but density modification and autotracing often fails to reveal the rest of the structure. The process stalls as no additional features develop in the map, whether in the extension of the polypeptide chain or in side chain electron density. SEQUENCE SLID-ER is being developed to extend the initial and intermediate partial models by assembling multiple models from the most probable side chains into the current fragments. As secondary structure prediction of residues from sequence is reliable, this information is used to restrict possibilities matching the secondary structure of residues of the partial model and traces. Moreover, additional filters are applied based on free energy calculation using crystal contacts and assignment of hydrophobic and hydrophilic residues to protein cores and surface, respectively. Models with different side chain assignment are assembled with SCWRL4 [3] and may be modified with refinement. Extended partial structures with the best indicators are pushed on to density modification and tracing with SHELXE. Specific strategies of SLIDER have been designed within ARCIMBOL-DO SHREDDER and in the coil coiled mode. Three novel structures and other test cases determined with SLIDER are presented.

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MS42-P03

The expected log-likelihood gain for decision making in molecular replacement

Robert D. Oeffner¹, Pavel V. Afonine², Claudia Millán³, Massimo Sammito³, Isabel Usón³, Randy J. Read¹, Airlie J. McCoy¹

- Department of Haematology, University of Cambridge, Cambridge, United Kingdom
- Lawrence Berkeley National Laboratory, Berkeley, United States of America
- 3. Structural Biology, Molecular Biology Institute of Barcelona, Barcelona, Spain

email: rdo20@cam.ac.uk

Protein crystallographers often make assumptions about the solvability of a structure by molecular replacement based on two variables: the sequence identity between the model and target and the resolution of the data. We have recently shown that the solvability of a structure by molecular replacement is, rather, predominantly dependent on four variables: the number of reflections in the data set, the fraction of the scattering for which the model accounts, the RMSD between the model and target, and the measurement errors in the data. Furthermore, the solvability can be quantified with the eLLG (McCoy et al., 2017, Oeffner et al., 2018). The eLLG is the LLGI (Read & McCoy, 2016) expected from a correctly placed model, calculated as a sum of log-likelihoods of each reflection predicted by the model but offset by the sum of log-likelihoods of a model of random atoms. Using the eLLG, the crystallographer can judge whether to pursue molecular replacement or attempt experimental phasing as the quickest path to structure solution. Other applications of the eLLG include determining search order; finding the minimal data requirements for obtaining a molecular replacement solution using a given model; and for decision making in fragment based molecular replacement, in single atom molecular replacement, and for likelihood-guided model pruning.

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Keywords: Likelihood, eLLG, LLGI

MS42-P04

jsCoFE, a cloud system for crystallographic computations from CCP4

Eugene Krissinel¹, Andrey Lebedev¹, Charles Ballard¹, Ville Uski¹, Ronan Keegan¹

1. CCP4, Research Complex at Harwell, STFC-RAL, Didcot, United Kingdom

email: eugene.krissinel@stfc.ac.uk

The Collaborative Computational Project Number 4 in Protein Crystallography (CCP4) exists to maintain, develop and provide world-class software that allows researchers to determine macromolecular structures by X-ray crystallography and other biophysical techniques. Over 37 years, the CCP4 Software was assembled and distributed as an integrated Suite of programs, installable on either user's personal PCs or centralized facilities.

Modern trends in computing suggest a fast-growing interest to mobile platforms and cloud solutions for data storage and operations in practically all areas. In context of crystallographic computing, cloud solutions become increasingly appealing in view of recent advances in automated structure solution methods, which demand for both computing power and various databases makes them less suitable for offline (local) setups. Another appealing feature of the cloud model is the simplification of software and data management, both for software provider/maintainer and end users.

Over last decade, CCP4 have developed web services for automated structure solution, which are available to crystallographic community online. In this communication, we report on the development of isCoFE (Javascript-powered Cloud Front-End), which expands CCP4 web-services to potentially all functional CCP4 components and allows a user to keep and operate their data and whole structure solution projects on-line. jsCoFE works on all computing platforms capable of running ordinary web-browsers (including smartphones and tablets), and does not require any local data storage. Currently available functionality, apart from automated solvers, includes data merging and scaling, phasing (MR and EP), density modification, model building, refinement, ligand fitting and structure analysis. Experimental data may be either uploaded from user's device or obtained directly from data producing facility, such as a synchrotron, online (currently limited to Diamond Ltd). Visualisation tools include UglyMol and Coot, which can be also used for model building and coordinate manipulations.

Technically, jsCoFE represents a network of web-servers, which includes head node(s) for keeping user projects and overall data logistics, and computational node(s) for performing actual computations. Owing the exclusive use of http(s) protocol for all communications within jsCoFE, there is no principal restriction on geographic location of any of the nodes, which makes the system almost infinitely scalable. In the opposite extreme, all nodes may be allocated on a single machine, then jsCoFE represents itself as a mere GUI.

jsCoFE is accessible at http://ccp4serv6.rc-harwell.ac.uk/ jscofe/ and is available for custom installations ranging from individual desktops to central locations such as a laboratory, University/Institute or a synchrotron.

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Krissinel, E., Uski, V., Lebedev, A., Winn, M. & Ballard, C. (2018) Distributed Computing for Macromolecular Crystallography, Acta Cryst D 74(2), 143-151

Keywords: WWW, Computing, Crystallography

MS42-P05

X-ray crystallography to cryo-electron microscopy: computing infrastructure in structural biology

Jason Key¹, Peter Meyer¹, Carol Herre¹, Michael Timony¹, Dimitry Filonov¹, Justin O'Connor¹, Piotr Sliz¹

1. Biological Chemistry and Molecular Pharmacology, Harvard Medical School, Boston, United States of America

email: key@hkl.hms.harvard.edu

SBGrid is an academic research group based at Harvard Medical School dedicated to structural biology computing. Started in 2000, the group's primary initiatives are the SB-Grid consortium, a software collaborative of more than 320 structural biology labs in 20+ countries (Morin, 2013), and the SBGrid DataBank which was established in 2015 as an open research data publication system for the Structural Biology community (Meyer, 2016). The SBGrid consortium provides a supported collection of scientist-created software titles for Crystallography, NMR, Electron Microscopy, Computational Chemistry, and Structure Visualization & Analysis with workshops and webinars to connect scientists with the scientist-developers who create the software. SBGrid DataBank supports validation and reproduction of macromolecular models and development of structural biology processing methods (Meyer, 2016). It currently contains primary data sets supporting over 400 macromolecular structures. Recent advances in cryo-electron microscopy (cryo-EM) detector technology have resulted in an increasing number of X-ray crystallographers turning to cryo-EM to determine structures of biological macromolecules too intractable or too difficult to determine by crystallographic techniques. The computational infrastructure used to support x-ray crystallography is only marginally capable supporting cryo-EM computations. In particular, efficient cryo-EM computation requires more, and higher performance storage; and places significant emphasis on GPU computation. Additionally, the general principles that making primary data available supports structural validation and methods development applies even more significantly to cryo-EM than it has with x-ray crystallography. Here we will present how various parts of SBGrid infrastructure including software, data management tools, as well as local and cloud high performance computing resources contribute to establishing a robust support for crystallography and cryo-EM experiments.

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Keywords: Cryo-EM, Computing, GPU

MS44- Operando and in-situ crystallographic studies using powder diffraction

Chairs: Prof. Simona Galli, Dr. Gavi Vaughan

MS44-P01

Structural and spectroscopic investigation on the crystallization behavior of Bi₂Fe₄O₉

Andrea Kirsch¹, M. Mangir Murshed¹, Thorsten M. Gesing¹

 University of Bremen, Solid State Chemical Crystallography, Institute of Inorganic Chemistry and Crystallography, Leobener Str. 7, D-28359, Bremen, Germany

email: a.kirsch@uni-bremen.de

Materials in the nano-sized regime often show unique and size-dependent properties. Despite intense studies on nanomaterials a systematic structural and spectroscopic study on a given system and the associated size-dependent physical properties is rarely studied, in particular from nano-crystalline into poly-crystalline (bulk) material through a critical size-regime. We carefully investigate the crystallite size-dependent structural features of Bi₂Fe₄O₉ ex-situ as well as in-situ. Temperature-dependent X-ray powder diffraction (XRPD) on an X-ray amorphous precursor of Bi2Fe4O9 stoichiometry revealed that both (Bi1xFex)FeO3 and Bi2Fe4O9 simultaneously crystallize from 780 K on, and the perovskite phase transformed into Bi₂Fe₄O₉ above 860 K. Thus, heating the precursor above this point for 2 h at a subsequent higher temperature produces pure Bi2Fe4O9 samples with greater average crystallite sizes. As such, twelve samples with different crystallite sizes from 35.3(4) nm to 401(17) nm were produced using the temperatures between 900 K and 1073 K. Rietveld refinements on X-ray powder data collected at ambient condition ex situ showed that the lattice parameters depend on the crystallite size; similar to the trend observed for the evaluated data of the in-situ XRD measurements. Significant changes of the lattice parameters are caused by strong distortions of the FeO4 tetrahedra and cooperative rotation of the FeO6 octahedra. Analyses of the widths and frequencies of the Raman modes support these structural features. The electronic bandgap and the 2nd absorption edge observed at around 700 nm are found to be a function of the crystallite size. Why the Urbach energy steeply drops down from 0.33 eV to 0.19 eV at the crystallite size of 64 nm leaves an open question, which is the critical length of the magnetic cycloidal spiral of the multiferroic BiFeO31.

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Keywords: nanocrystalline, size-dependent properties, Bi2Fe4O9

MS44-P02

Crystal Structures of Solid Fluorine and Nitrogen Trifluoride

Sergei Ivlev¹, Antti Karttunen², Markus Hölzel³, Florian Kraus¹

- 1. Fachbereich Chemie, Philipps-Universität Marburg, Marburg, Germany
- 2. Department of Chemistry and Materials Science, Aalto University, Aalto, Finland
- 3. Forschungs-Neutronenquelle Heinz Maier-Leibnitz, Garching, Germany

email: sergei.ivlev@chemie.uni-marburg.de

The crystal structures of the chemical elements belong to the fundamental knowledge of chemistry as atom distances, bond lengths and angles can be determined precisely and the data serve as benchmarks for quantum chemistry. Surprisingly, the crystal structures of α -fluorine and β -fluorine have so far only once been investigated [1,2]. Probably this is due to the fact that solid F₂ is still extremely reactive and in the case of α -F₂ the authors reported several explosions due to the highly exothermic phase change and the subsequent reaction of F₂ with the sample holder [1]. It was concluded that α -F₂ crystallizes in the monoclinic crystal system, probably in space group type C2/m, but space group type C2/c could not be ruled out. Later the original diffraction data were reinterpreted by others and space group C2/c was found to be more likely correct [3]. The precise space group of α -F₂ remained, however, uncertain, which naturally has an influence on the determined atom positions, bond lengths and displacement parameters. The crystal structure of β -F₂ was first reported in 1964 and determined by means of single crystal X-ray diffraction [2], the problem to distinguish between two cubic space group types, P-43n and Pm-3n, was faced. The higher symmetric space group type was chosen since a disordered structure was expected. Neither the bond length of the F2 molecules, and not the anisotropic displacement parameters of the fluorine atoms could be refined

Therefore, we constructed a gas line attached to a sample holder inside the SPODI neutron diffractometer at the FRM-II neutron facility of the Heinz Maier-Leibnitz Zentrum in Garching, Germany. The crystal structures of α - and β -fluorine were determined using powder neutron diffraction and Rietveld refinement. We will report on the obtained models providing much more precise lattice parameters, atomic coordinates as well as bond lengths for the two polymorphs of fluorine. Using the same gas line we attempted an elucidation of the previously unknown crystal structure of solid nitrogen fluoride at various temperatures.

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Keywords: fluorine, nitrogen trifluoride, neutron diffraction

MS44-P03

Yttrium substituted Bismuth oxides as high-temperature thermochromic materials

Thorsten M. Gesing1-2, Anne Staubitz 1-2, Xi Liu1

- 1. University of Bremen, Institut of Inorganic Chemistry and Crystallography, Bremen, Germany
- 2. MAPEX Centre for Materials and Processes, Bremen, Germany

email: gesing@uni-bremen.de

Polymorphs of bismuth oxide and its yttrium substituted solid solutions (Bi_{1-x}Y_x)₂O₃ (0.00 £ x £ 0.25) exhibit excellent thermochromic properties in the range from room temperature to 1050 K. The colors change mostly from yellow at low temperatures to various brown hues at high temperatures. The compounds in this nominal series were examined between 293 K and 1050 K using X-ray powder diffraction, UV-Vis spectroscopy, and dynamic scanning calorimetry. A combination of Tauc and DASF methods were applied to determine the band gap energies and types from the diffuse UV-Vis spectra for these semiconducting oxides. It is well known that reversible monoclinic (low temperature) to defect fluorite-type cubic (high temperature) or tetragonal (low temperature) to defect fluorite-type cubic (high temperature) phase-transitions occur on heating and cooling for pure bismuth oxide and the solid solution with 10% cation substitution, while none in the solid solutions with x > 0.1without annealing. Thermochromic behavior is observed for all samples studied in this series to be generally a gradual darkening as the temperature increases at the regions without any phase transitions, and a more abrupt color change at the stage where a phase-transition happens (Figure 1). The UV-Vis reflectance spectra show the room-temperature absorption edges of all samples in the range between 2.4 eV to 2.8 eV. The spectrum of pure a-Bi2O3 show a sharper threshold at the absorption edge comparing to the rest samples, which contain high concentration of vacancies on the anion sites. At higher temperatures, the absorption edges extend into longer wavelength regions, resulting in darker colors.

Figure 1: Optical color change of $(Bi_{0.95}Y_{0.05})_2O_3$ between 300 k and 1050 K.



Keywords: thermochromic materials, high-temperature powder diffraction, phase-transition

MS44-P04

HEIMDAL@ESS – Fast neutron powder diffraction for material science

Jürg Schefer¹, Jonas Birk², Sonja L. Holm², Dan Mannix³, Kåre Iversen³, Rodion Kolevatov⁴, Bjørn Hauback⁴, Kim Lefmann², Lukas Keller¹, Mogens Christensen³

- 1. Paul Scherrer Insitut, Villigen PSi, Switzerland
- 2. Nanosicience Center, Niels Bohr Institute, University of Copenhagen, Copenhagen, Denmark
- 3. Departement of Chemistry & iNano, University of Aarhus, Lund and Aarhus, Sweden
- 4. IFE, Institute for Energy Technology, Kjeller, Norway

email: jurg.schefer@alumni.ethz.ch

New functional materials are in the focus for cutting-edge materials as demanded for example to minimize energy consumption, reducing waste and optimizing recycling processes. Such new materials must be probed under working conditions by a wide range of methods including neutron diffraction, covering a length scale from millimeters down to atomic distances below <1 nm.

The HEIMDAL [1,2] instrument at the new spallation neutron source ESS is exactly covering these needs, combining powder diffraction (NPD), small angle scattering (SANS) and neutron imaging (NI) in a single instrumental setup. It is essential to have time dependent information from the sample using different probes to give access to all length scales. In a first stage, we will complete the powder diffraction part, later upgrade the instrument by the SANS and imaging option.

A key component of the instrument is a double guide delivering thermal and cold neutrons. Extracting neutrons through two separated guides was a consequence of the different optics needed for the transport of cold and thermal neutrons, respectively. Our solution allows the optimization of the flux-sensitive NPD using thermal neutrons down to 0.5Å. The NPD takes full advantage of the long pulse of ESS: HEIMDAL can deliver high flux as well as high resolution by adjusting the pulse width within seconds. We can adapt exactly to the need for the materials science community, where phase transitions and structural parameters can be envisaged.

As we expect a less trained user community in this field, we and the Data management and software center (DMSC) in Copenhagen will make a big effort to offer a wide range of easy-to-operate software packages, such as 2D Rietveld refinement.

Figure 1:

The layout of the new HEIMDAL instrument at the European Spallation Neutron Source ESS in Lund, Sweden: A dedicated instrument for *in-situ* and *in-operandi* studies for materials science in the long experimental hall.



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Keywords: Neutron Diffraction, In-Operandi, In-Situ

MS44-P05

Temperature-dependent structure changes of complex aluminium hydrides with Rb and Cs as metal cations

Claudia Weidenthaler1, Simone Gallus1

 Max-Planck-Institut f
ür Kohlenforschung, Department of Heterogeneous Catalysis, M
ülheim an der Ruhr, Germany

email: weidenthaler@mpi-muelheim.mpg.de

Complex aluminium hydrides are interesting materials with respect to the release and uptake of hydrogen. Since hydrogen is part of the crystal structure of the hydrides, such compounds can serve as solid hydrogen storage materials. The temperature dependent behaviour of most of the complex aluminium hydrides with alkali and earth alkaline metals has been studied intensively.[1] The crystal structures of complex aluminium hydrides are built from isolated [AlH₄]tetrahedra which coordinate the metal cations. The decomposition of aluminium hydrides with alkali metals proceeds via the formation of intermediate hexahydride structures consisting of isolated [AlH₆]²⁻ octahedra. This formation is associated with a first hydrogen release step before simple metal hydrides form after a second step. However, in situ X-ray diffraction experiments have shown that their decomposition route cannot easily be transferred to CsAlH₄ and RbAlH₄.^[2] The transformations are more complex and do not proceed via the known hexahydride structures. In situ synchrotron measurements have been performed in order to study the processes and the phases formed during the dehydrogenation of both hydrides.

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Keywords: complex aluminium hydride, hydrogen storage, in situ powder diffraction

MS44-P06

Low temperature X-ray investigations using a Guinier diffractometer system

Michael Tovar¹, Galina Gurieva¹, Susan Schorr²

- 1. Helmhotz-Zentrum Berlin, Berlin, Germany
- 2. Helmholtz-Zentrum Berlin / Freie Universität Berlin, Berlin, Germany)

email: tovar@helmholtz-berlin.de

Using a Guinier diffractometer for low temperature X-ray diffraction allows accurate investigations of lattice parameters at non-ambient conditions. Therefore, we are able to trace subtle changes in cell metrics such as cell parameter deviations or symmetry breaking. In this contribution, we will apply this technique particularly to kesterite-type solar absorber materials. For Kesterite-type materials unusual thermal behaviour like negative thermal expansion is reported (1). Measurements from 10 to 300 K were collected. Description of the instrument and outcome of low temperature X-ray investigations will be presented and compared to formerly results.



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Keywords: Low temperature, Guinier, Phase transition

MS44-P07

Structural Properties of (Ce,La)Pd₂Al_{2-x}Ga_x Compounds

Petr Doležal¹, Dominik Kriegner¹, Milan Klicpera¹, Alexandra Rudajevová¹, Jiří Prchal¹, Pavel Javorský¹

1. Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic

email: petr284@seznam.cz

(Ce,La)Pd₂(Al,Ga)₂ are intermetallic compounds with a tetragonal CaBe2Ge2 structure type at room temperature. This structural type is very common in intermetallic compounds with a 1:2:2 stoichiometry. The studied compounds undergo a structural phase transition at low temperatures. The low temperature structure of CePd₂Al₂ is orthorhombic (Cmme) below 13.5 K [1] and CePd₂Ga₂ is triclinic below 125 K [2]. Similar structural behaviour is observed in their non-magnetic La analogues. It is not known what causes the different behaviour of CePd2Al2 and CePd2Ga2 compounds at low temperatures considering the room temperature structure is similar for both compounds. The CePd₂Al₂ is also one of the rare examples of Ce-based compounds whose magnetic excitations in crystal electric field does not fulfil the scheme based on a tetragonal point symmetry of the Ce ion [1].

In the presented study we focus in more detail on the structural properties of the (Ce,La)Pd_2Al_2,Ga, series using the low temperature X-ray powder diffraction. These results are also compared with inelastic neutron spectra, which shows the behaviour of magnetic excitations in this series. We found that specific Ga concentration leads to the suppression of the transition temperature in the CePd_2Al_2,Ga, series. We also studied the structural transition on CePd_2Al_a and LaPd_2Al_2 single crystals which were prepared by using the Czochralski method.

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Keywords: low temperature structure, structural phase transition

MS44-P08

Beamline P02.1: a workhorse for highresolution powder diffraction & total scattering experiments at PETRA III, DESY

Michael Wharmby¹, Martin Etter¹, Jozef Bednarcik¹, Jo-Chi Tseng¹, Mario Wendt¹, Sergej Wenz¹

1. P02.1, PETRA III, DESY, Hamburg, Germany

email: michael.wharmby@desy.de

Powder diffraction is a standard tool for characterisation in a wide range of fields across the physical sciences: from materials science and metallurgy, to chemistry and solid state physics. Third generation synchrotron sources provide high fluxes of X-rays at higher energy than laboratory sources. These characteristics open the door not only to rapid data collection for high spatial-resolution structural studies, but also to time-resolved in situ/in operando measurements of functional materials under real conditions, thanks to high energy X-rays being able to penetrate operating environments. Furthermore, the use of high energy X-rays increases the region of reciprocal space which may be studied in an experiment, facilitating improved spatial resolution in total-scattering measurements.

Beamline P02.1 (PETRA III, DESY, Hamburg, Germany) is almost unique amongst high-resolution powder diffraction instruments in operating at a fixed energy of 60 keV [1],[2]. This energy is particularly well suited to the collection of powder diffraction data for Rietveld refinement (especially for high-Z materials, where absorption is a problem at lower energy) and for collection of total-scattering data (the high energy facilitating Q_{Max} of at least 20 Å⁻¹), which may be interpreted by Pair Distribution Function (PDF) analysis. Currently two detectors are available on the beamline (a two-dimensional Perkin Elmer XRD1621 and an in-house developed 10-channel Multi-Analyser Detector), whilst additional devices are available from a shared detector pool (including a Dectris Pilatus3 CdTe 2M designed for high-energy data collection).

In addition to ambient temperature capillary measurements, P02.1 offers a range of standard sample environments (e.g. hot-air blower - RT-1100 K; cryostream - 90-500 K; cryostat - 10-300 K) whilst a number of others are under development (e.g. low pressure gas adsorption cell) or are maintained by the PETRA III sample environment group. Recently we have also brought a sample changing robot into operation, with capacity for 300 samples; this device is compatible with the cryostream and hot-air blower environments. Furthermore, the enormous amount of free space around the diffractometer, compared to many other powder diffraction beamlines, allows easy integration of complicated sample environments which are brought to the beamline by our users. We report here the latest developments at P02.1 including planned changes to detector configurations, new sample environments, updates to the control software and possible remote access schemes.

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MS44-P09

Impact of tempering temperature on the properties of steel: An in-situ X-ray diffraction study

Andreas Pein1, Manfrad Wiessner

1. Anton Paar GmbH, Graz, Austria

email: andreas.pein@anton-paar.com

Material properties are strongly dependent on the structure and arrangement of the

atoms / molecules of which the material is comprised. For **steel**, different properties are required for the wide range of possible applications. Heat treatment (tempering) can be used to alter the microstructure and phases present within the steel and, therefore, change the material properties. In-situ X-ray diffraction measurements can be used to study these changes.

The mechanical properties of soft martensitic steels, which find use in a wide variety of applications, are strongly dependent on the microstructure which develops during heat treatment. After treatment, the steel consists of different phases; typically a combination of martensite, reverted or retained austenite, and carbide precipitates. Reverted austenite is the austenite which forms at sufficiently high temperatures during the tempering process.

Some superior properties found in these steels are high values in both fracture toughness and impact strength. These are caused by the microstructural arrangement of reverted austenite and martensite. It is therefore clear that the mechanical properties of the steel are dependent on the heat treatment as this influences the development of different phases and the microstructure within the steel.

In order to identify the effect of tempering temperature on the mechanical properties, in-situ high temperature X-ray diffraction is employed to study the microstructural changes occurring during tempering (1). This includes following the formation of different phases, as well as monitoring the dislocation densities; these can then be related to mechanical properties such as the impact strength and tensile strength. In this way, an improved understanding can be developed to optimize the tempering process in order to obtain steels with the desired properties.

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[1] Wiessner, M. et al. (2017) Materials Science & Engineering, A682, 117-125

Keywords: in-situ X-ray diffraction, steel, copper tempering

GI-MS45- Women in crystallography

Chairs: Dr. Julia Contreras, Dr. Annalisa Guerri

GI-MS45-P01

Women under high pressure

Julia Contreras1, Miriam Peña2, Shanti Deemyad3

- 1. CNRS-Sorbonne Université, Paris, France
- 2. SUPA, Edimburgh, United Kingdom
- 3. Utah University, Utah, United States of America

email: julia.contreras.garcia@gmail.com

This is an initiative to highlight the (rising) number of women working in the high pressure research field. We come from all domains (geology, biology, physics, chemistry...). Indeed, we are not many, but we are many more than many people think. We are building up a public data base of women under high pressure group. We are several scientist women who work in the high pressure field. http://www.lct. jussieu.fr/pagesperso/contrera/index-hp.html

We have also created a FB and twitter accounts for everybody to be able to follow updates:

h t t p s : / / w w w . f a c e b o o k . c o m / W H P -1731930103697127/?code=95036

The aim of our group is to provide the community with facilities to count with gender equality at any of the high pressure events and lists. It has also helped organizers of events and committees to have a fair gender representation and provide a great example of women in science and references to many women graduate students and postdocs in the audience.

We are trying to get as visible as possible not to be complainers and neither to build up a "women" club, our goal is to bring awareness and make us think twice in order to create a fair gender community.

References:

http://www.lct.jussieu.fr/pagesperso/contrera/index-hp.html

Keywords: women in science, high pressure

GI-MS48 - Education in crystallography

Chairs: Prof. Mike Glazer, Dr. Aleksandar Visnjevac

GI-MS48-P01

How symmetry in the islamic ornament can be relevant to introduce symmetry in the crystallography teaching.

Youssef Aboufadil¹, Abdelmalek Thalal², My Ahmed Elidrissi Raghni², Abdelaziz Jali²

- 1. Department of physics, Polydisciplinary Faculty of Safi, Marrakech-Safi, Morocco
- 2. Department of physics, Faculty of Sciences Semlalia marrakech, Marrakech, Morocco

email: youssefaboufadil@yahoo.fr

Crystallography uses the most elementary expression of symmetry, the visual one of geometry whose elements are the isometries of the Euclidian space: inversion, rotation, reflexion in a mirror, plus the translation in space, ideal crystal being supposed infinite. Mathematically, an object is symmetric if it remains invariant under the application of a set of isometries called symmetry group.

The drawings of Escher [1] are crystallographic classics in teaching two-dimensional space groups. Due to the biological nature of the interlocking objects in them, they are most appealing in the cases of the lower-symmetry groups. The other man-made two-dimensional periodical patterns suitable for the study of plane groups are primarily the Roman, Byzantine and Romanesque mosaics, and the gothic. Especially suitable, however, is the large group of Islamic geometric patterns, executed in tilework, brickwork, stucco, wood, marble and metal [2].

In Islamic ornaments, we encounter two types of symmetry groups:

1. Finite group: cyclic group C_n (Figure 1) and dihedral D_n (6 <= n <= 96) (figure 2) called groups of rosettes,

2. Infinite space groups: group of friezes in one-dimensional space (1D) and wallpaper group or crystallographic planar groups in two-dimensional space (2D).

The Islamic geometric patterns best suited for teaching come from linear drawing, the multi-coloured and interlaced patterns (Figure 2). Introduction of colour and interlaces introduce additional elements of complexity and subtlety in the decorative patterns. To rigorously describe the intertwined and coloured patterns, large number of groups are deduced from the parent plane groups [3]. Moreover, the order-disorder and quasiperiodic structures encountered in Islamic ornaments may facilitate the approach of structures in crystallography.

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Keywords: symmetry, teaching, Islamic ornament.

GI-MS48-P03

Exploring structural biology on the web: to biologists and beyond

David Armstrong1, Sameer Velankar1

1. PDBe, EMBL-EBI, Cambridge, United Kingdom

email: davida@ebi.ac.uk

Teaching macromolecular structure is often complicated by the need to have specialist tools to view structures and related information. At the PDBe we have integrated a number of different components that allow easy visualisation of structural data in different ways within the web browser.

These components include lightning-fast molecular visualisation with LiteMol and a sequence component to link this visualisation to the primary structure, via secondary structure topology diagrams. These interactive components enable students to explore sequence information and its relationship to 3D structure. The components integrate extra annotations including domains and validation data. Visualisation of electron density maps within LiteMol makes it an excellent tool for introducing students to the importance of validation in structural biology.

All of these components operate within a browser window, including on mobile devices, meaning that they are available to anyone, anywhere. This has enabled us to effectively teach macromolecular structure to students at all levels and even to introduce structural biology to artists and the wider general public. We hope this will help to bring structure to biology and beyond.

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Mir, S. et. al. (2018) Nucleic acids research, 46, D486-D492 Sehnal, D. et. al. (2017) Nature methods, 14, 1121-1122

Keywords: Visualisation, Sequence to structure, validation

GI-MS48-P04

A model description of crystalline state under external influences

Boris Kodess1, Pouline Kodess2

- 1. CMD, Materials Science VNIIMS-ICS&E, Moscow, Russia
- 2. Materials Science Dept. ICS&E, Aurora, CO, United States of America

email: kodess@mail.ru

A method is proposed for describing the change in the ground state of a phase of a crystalline substance under external influences. This manner of expression takes into account the multifactorial nature of governing factors which determine phase transitions and influence the functional characteristics of the materials being created from the substances. The phase space for crystals is constructed vector interactions) using three basic and enough independent factors and then associated with the composition of substance. They describe, first, the change in the level of available potential or the incoming energy to the substance; second, the time characteristics, included for describing emerging and existing phases; third, the spatial localization of the phase, respectively.

For a more detailed description of the processes of phase state change under external influences these factors consistently combine into the factors of the second level, which create subsystems to describe the origin of space-time patterns, the evolution of the state of the phase, and third, to describe the phase transitions in substances. Then a subsequent combination of all three specialized second-level factors in the third-level factors makes it possible to describe the relationship of changes in composition and structure with functional characteristics that reflect the generalized information nature of these characteristics; this can be used to describe more complex behavior, for example, temporal oscillations of all structural parameters in certain inorganic, usually multi-component substances.

The use of the model in educational practice has shown that the proposed method of description of a crystal phase state is useful for a more accessible and comprehensive, and also for a wider explanation of the multifactor nature of characteristics of condensed substances in the crystalline state. The model also ensures a better transfer of the accumulated knowledge about the specific features of the crystalline state into the processes of creating and developing new types of crystals and the technologies for the production and processing of materials, necessary for use in various spheres of life and industry.

The connection of this model with fundamental physico-chemical concepts can be useful for students as a new tool for deeper and successful mastering of crystallography. We noticed [1-3] that students whose crystallographic interests are related to the functional information properties of substances based on the key factors of the crystalline state, faster socialize in the modern information society and more confidently and reliably solve specific problems in the field of materials science.

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Keywords: model crystalline state, factors of phase space, students' comprehension

GI-MS48-P05

The crystallization competition in the school: an innovative teaching/outreach tool for secondary schools

Juan Manuel Garcia Ruiz¹, Alfonso Garcia Caballero¹, Fernando J. Lahoz², Miquel Àngel Cuevas Diarte³

- 1. Laboratorio de Estudios Cristalográficos (IACT, CSIC-UGR), Granada, Spain
- Instituto de Síntesis Química y Catálisis Homogénea (CSIC-Universidad Zaragoza), Zaragoza, Spain
- Departamento de Cristalografía y Mineralogía (Universidad de Barcelona), Barcelona, Spain

email: juanmanuel.garcia@csic.es

The 'Crystallization Competition in the School' is a teaching/outreach activity aimed at students aged 12-17, whose main goals are to disseminate the importance of crystallography and crystallization and inspire scientific vocations. Since it was first organised in 2009/2010 (Andalucia/Puerto Rico), the popularity of the Competition has quickly spread across Spain. In this school year (2017/2018), eight editions have been organised in different regions of Spain, counting with the direct participation of 282 schools, 495 teachers and 7,768 pupils.

The format of the Competition is intended to provide school students the experience of being a 'real' scientist: from designing a scientific project, through working in practical crystallization experiments and keeping a laboratory notebook, putting into practise their presentation skills and sharing outcomes with scientists and fellows from other schools. This innovative approach is implemented in three successive stages that place teachers at its heart in order to engage with the entire educational community. At the first stage, teachers are trained in fundamental crystallography and crystallization concepts through the organisation of a practical workshop that provides them with teaching tools and resources that can be turned into enjoyable activities for the classroom. In the second stage, students develop a laboratory project under the supervision of their teachers making use of a motivating crystallization kit of ammonium dihydrogen phosphate (ADP) that enables them to stir their scientific imagination and bring out their scientific spirit. Students can also develop other types of projects such as crystallization of salts by cooling, formation of geodes and crystallization in gels. The final phase of the Competition is organised similarly to a scientific conference, where students make the presentation of a poster, their grown crystals and a lab notebook that is evaluated by a panel of scientists. By the end of the Competition, students will have learnt to behave as 'scientists' and developed work-related scientific values such as observation, systematic study, rational thinking, teamwork and communication skills.



References:

http://www.lec.csic.es/concurso/

We would like to acknowledge the contribution of the chairpersons of the different regional contests: Martha Santana Ibáñez (MS Services Granada, Andalucía); Sol López de Andrés (Universidad Complutense, Madrid); Begoña Bazán Blau (Universidad del País Vasco, País Vasco); Jesús Berenguer (Universidad La Rioja, La Rioja); Manuel de Pedro del Valle (Universidad de Cantabria, Cantabria); Maria Jose Ruiz García (Universidad de Castilla La Mancha, Castilla La Mancha), Pilar Gómez Sal (Universidad de Alcalá de Henares, Madrid), Vicente Pelegero García (Ciudad de la Artes y las Ciencias, Valencia), Vicente Esteve Cano (Universidad Jaume I, Castellón).

Keywords: Competition, Crystallization, Teaching

GI-MS48-P06

Symmetry groups in the islamic geometric art: ornamental patterns of Konya (Turkey) and Marrakech (Morocco)

Abdelmalek Thalal¹, Semra Ide², Youssef Aboufadil³, Nermin Şaman Doğan², Yunus Koc²

- 1. Department of physics, Faculty of Sciences Semlalia Marrakech, Marrakech, Morocco
- 2. Hacettepe University, Ankara, Turkey
- 3. Department of physics, Polydisciplinary Faculty of Safi, Cadi Ayyad University, Marrakech, Morocco

email: abdelmalekthalal@gmail.com

Since the Middle Age, Muslim world has a great artistic and decorative tradition. In this vast space which were spread from Africa to Asia through Andalusia, there are treasures of unmatched beauty in the Islamic geometric art.

The skill of the master craftsmen, their knowledge of the concept of symmetry have allowed the development of this art over the centuries [1]. Indeed, symmetry is an essential tool in conceiving the ornamental patterns, regardless of their degree of complexity.

Since the end of the 19th century, many authors have been interested in Islamic ornamental motifs. In 1879, Bourgoin compiled nearly 200 geometric patterns. The development of group theory in the 20th allowed the analysis and classification of these motifs from the point of view of symmetry. Some authors [2] have attempted to find the 17 crystallographic groups of the plane established by Fedorov. Other authors have used computer to generate ornamental patterns. Finally, the advent of quasicrystals has led scientists to study some Islamic ornamental patterns as a quasiperiodic tiling [3].

Our purpose, in this presentation, is to study the symmetry in the ornamental art of the Eastern and Western Muslim world. We consider the geometric ornamental patterns found in two millennia cities, Marrakech and Konya, founded respectively by the Almoravid in Maghreb, and the Seljuk in Asia. The richness of the ornamental patterns achieved on several supports (stone, ceramic, wood, plaster,) allows an easy approach of the plane crystallographic groups, perfectly suitable for the introduction of group theory in crystallography.



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31st European Crystallographic Meeting • Oviedo, Spain 22-27 August

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Keywords: Symmetry, crystallographic groups, Islamic geometrical art

Late Abstracts

31st European Crystallographic Meeting

MS01 - Micro & nano crystals in MX

Chairs: Dr. Helen Ginn, Dr. Thomas White

MS01-P06

New Beamlines for Macromolecular Crystallography at MAX IV

Thomas Ursby¹, Mikel Eguiraun¹, Ana Gonzalez¹, Andrea Gross¹, Gustavo M.A. Lima¹, Jie Nan¹, Anastasya Shilova¹, Johan Unge¹, Uwe Mueller¹

1.(MAX IV Laboratory, Lund University, Lund, Sweden

email: thomas.ursby@maxiv.lu.se

MAX IV is the first operational 4th generation storage ring offering synchrotron radiation for many scientific communities. Among the first beamlines in user operation, BioMAX, the first macromolecular crystallography (MX) beamline, can be used to create high resolution 3D data from crystalline macromolecules to better understand the structure functional relationship of this complex matter. BioMAX has been designed as a work horse beamline to support all kinds of established crystallography methodologies and runs at a high automation level. The experimental station is equipped with a MD3 micro-diffractometer, an Eiger 16M hybrid pixel detector and an ISARA sample changer, which allows for complete data collections in seconds.

Recently a second MX beamline has been funded by the Danish Novo Nordisk Foundation. MicroMAX will become a micro-focusing beamline, which will allow for investigating micrometer sized protein crystals at room temperature using serial crystallography. Here the complete diffraction dataset is composed of several thousand single frames, partial datasets of a large number of crystals. Using a wide bandpass option, MicroMAX can be exploited also for time resolved crystallography down to the microsecond time resolution range. After a four-year construction period, the beamline will be ready for first experiments.

Keywords: Beamlines, Macromolecular crystallography, Serial crystallography

MS02 - From data collection to structure finalization: getting the most from you<u>r crystal</u>

Chairs: Dr. William Shepard, Dr. Katherine McAuley

MS02-P14

Scaling data in the DIALS framework

James Beilsten-Edmands¹, Richard Gildea¹, Ben Williams¹, David Waterman¹, Gwyndaf Evans¹, Graeme Winter¹

1. Diamond Light Source Ltd, Chilton, Didcot, United Kingdom

email: james.beilsten-edmands@diamond.ac.uk

The process of scaling crystallographic data aims to put all reflections on a common scale, by correcting for experimental effects such as sample illumination, absorption and radiation damage. Here we present the implementation and evaluation of a new scaling framework in the DIALS diffraction integration package[1], for scaling of macromolecular and chemical crystallographic data. We discuss the details of the scaling models used to correct the data and of the algorithm choices available. Our framework allows a new incremental workflow for multi-crystal scaling, allowing finer control of the scaling models for individual datasets, as well as further analysis tools for scaling model validation. We demonstrate the use of and the results of our scaling programs on a number of example datasets, including thin-wedge rotation data and weak-intensity data.

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Keywords: Scaling, DIALS

MS03 Combining methods in macromolecular structure determination, including special conditions MX

Chairs: Dr. Martin Walsh, Dr. Victor Lamzin

MS03-P07

Scanning electron diffraction reveals the crystalline microstructure of Cellulose Nano Crystals

Tom Willhammar¹, Duncan Johnstone², Yingxin Liu¹, Lennart Bergström¹, Paul A. Midgley²

- Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden
- Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom

email: tom.willhammar@mmk.su.se

All living plants contain cellulose as a crucial part of their structures. It possesses a complex structural diversity, including chirality. The combination of its fascinating structural features and its impressive properties in terms of specific strength and stiffness has triggered the engineering of cellulose-based materials with tailored mechanical and optical properties.

Scanning electron diffraction (SED) is an emerging method developed for the transmission electron microscope (TEM), following developments in electron optics and fast and sensitive detectors. By scanning a small electron probe, down to 1 nm in size, across the specimen and for each raster point a 2D electron diffraction pattern is acquired. In this way it is possible to build up a map revealing the ordering of the atoms in the sample with nanometer resolution. This method is opens up exciting opportunities for specimens, which are very beam sensitive and are difficult to study by other methods.

In this study, SED has been used to shed light on the microstructure of cellulose nanocrystals (CNCs) and to study the local ordering of the polysaccharide chains in the CNCs. Based on mapping of twisted CNCs it is possible to follow the ordering of the chains e.g. as the crystals are twisting.

Keywords: electron diffraction, cellulose, polymer

MS04 Biophysical characterization and crystallization

Chairs: Dr. Andrzej M. Brzozowski, Dr. Pavlina Rezacova

MS04-P14

Structural and biophysical characterisation of titin missense variants in genetic myopathies and cardiomyopathies

Roksana Nikoopour¹, Martin Rees¹, Mark Pfuhl¹², Ana Ferreiro³, Perry Elliott⁴, Mathias Gautel¹,

- Randall Division of cell and molecular biophysics, King's College London, London, United Kingdom
- 2. Cardiovascular Division, King's College London, London, United Kingdom
- Sorbonne Paris Cite, Universite Paris-Diderot, CNRS, Biologie Fonctionnelle et Adaptative UMR 8251, University Paris-Diderot, Paris, France.
- 4. Institute for Cardiovascular Science, University College London, London, United Kingdom

email: k1327385@kcl.ac.uk

Myopathies and cardiomyopathies are genetic conditions affecting skeletal and cardiac muscle. They are often caused by mutations in sarcomeric genes, such as TTN, which encodes the giant protein titin. Due to its size, TTN gene variants are also found in unaffected individuals (as shown by the 1000 Genomes Project) and it is difficult to assess their impact. In this project, biophysical techniques such as X-ray crystallography, differential scanning fluorimetry (DSF) and 1D Nuclear magnetic resonance (NMR) were applied to determine the structure of single and multiple titin A-band domains, in order to assess the impact of suspected and proven pathogenic variants on their stability and structure. Fibronectin type-3 domains from the titin A-band harbouring rare missense mutations were expressed in E. coli, both in wild-type (wt) and variant forms. All wt's were confirmed folded by NMR studies, whilst some variants had structural changes induced by the missense mutation. Their DSF melting temperatures were lower by around 10°C, suggesting a reduction in stability caused by the mutation as a common feature of genetically proven pathogenic TTN variants. X-ray structural data elucidated the structural basis of the destabilization, allowing visualization of impact of the missense mutation on the surrounding residues and tertiary structure of the protein.

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MS11 Hot structures in biology

Chairs: Prof. Maria Joao Romao, Prof. Fred Antson

MS11-P10

Structural studies of the five pilin proteins building up the type-V pilus Mfa1 of Porphyromonas gingivalis

Karina Persson¹, Michael Hal¹, Thomas Heidler¹, Yoshiaki Hasegawa²

1. Department of Chemistry, Umeå University, Umeå, Sweden

2. Department of Microbiology, Aichi Gakuin University, Aichi, Japan

email: karina.persson@umu.se

Structural and functional information of pili from the Bacteroidetes class of bacteria is sparse. Porphyromonas gingivalis, a periodontal pathogen belonging to the Bacteroidetes class, expresses two forms of pili, FimA and Mfa1. Each pilus consists of five proteins; FimA-E and Mfa1-5 respectively. Both represent the type-V form of pili. While the structure and assembly of type-1 pili from Escherichia coli is well studied, the chaperone-usher pathway, very little is known about the polymerization of type-V pili. In order to obtain an understanding of the structure, function and assembly mechanism of the P. gingivalis pili we have solved the X-ray crystal structures of all five Mfa proteins in recombinant form [1,2]. Despite low sequence similarity the Mfa1-4 proteins are structurally related to each other being built up from two β-sandwich domains. The P. gingivalis pilin proteins start as lipidated precursors before they are transported to the surface and polymerized. The precursor comprises an N-terminal extension, which is cleaved off upon polymerization. Intriguingly, all proteins were crystallized in their precursor forms with their N-terminal extensions still present. Part of this extension forms the first strand of the first β-sheet of the pilin. Maturation of the pilin is the result of cleaving the polypeptide at a conserved arginine downstream of this first β-strand resulting in a new N-terminus and a void in the first β-sheet. In analogy with the strand-displacement mechanism used for polymerization of the type-1 pili we believe that the void is filled by a donor β-strand from another pilin protein. However, despite having the crystal structure of all Mfa1-4 proteins and data from several mutagenesis studies we still do not know if it is the newly formed N-terminus or the long flexible C-terminus present on Mfa1 that constitute the donor strand.

The final protein, Mfa5, differs from the other Mfa proteins; it is much larger and consists of an N-terminal von Willebrand domain followed by a string of Ig-like domains [3]

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Keywords: pili, polymerization, bacteria

MS14 Combined approaches for structure characterization of modulated and complex structures

Chairs: Prof. Joke Hadermann, Dr. Phillipe Boullay

MS14-P05

Structural insights into the membraneanchored model of FtsQ/FtsB/FtsL complex in divisome

Claire V. Colin¹, Peng Zuo¹, Céline Darie¹, Holger Klein¹

1. Department of Chemistry, College of Natural Sciences, Seoul Natonal University, Seoul, Korea South

email: yuri93@snu.ac.kr

Bacterial cell division is a fundamental process that is initiated by FtsZ protein into a ring structure at midcell and facilitates a set of essential proteins known as the divisome [1,2]. Among them, the FtsQ/FtsB/FtsL complex was known as a scaffold protein connecting upstream and downstream division proteins. Despite previous intensive studies on the FtsQBL complex, the atomic details of the interface between FtsO and FtsB were not reported vet. To gain an insight into structural organization of the FtsQBL complex, we have determined the crystal structure of periplasmic domain of FtsQ in complex with C-terminal fragment of FtsB and showed that the C-terminal region of FtsB is a key binding region of FtsQ via mutational analysis in vitro and in vivo. Also, we proposed the model of FtsQ/FtsB/FtsL complex in curved membrane, with opposite N-terminal directions of FtsQ and the FtsB/FtsL complex via small-angle X-ray scattering and analytical gel filtration chromatography. These model suggests that the Y-shaped FtsQ/FtsB/ FtsL complex might fit well into the curved membrane for membrane anchoring during cytokinesis.

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Keywords: Divisome, Cytokinesis, FtsQ

MS20 Rating and improving data quality: instrumentation, analysis and postprocessing

Chairs: Dr. Karine Röwer, Dr. Loes Kroon-Batenburg

MS20-P14

The new chemical crystallography beamline at PETRA III

Martin Tolkiehn¹

1. DESY, Hamburg, Germany

email: martin.tolkiehn@desy.de

I will present the new beamline for chemical crystallography P24, which recwently started user operation at the high brilliance PETRA III synchrotron light source at DESY. The beamline is optimized for diffraction experiments with single crystals of small molecules. Measurements can be conducted at low and high temperatures in a large variety of sample environments including user supplied setups.

For highest flexibility two diffractometers with different geometries (heavy load Kappa and four circle Euler) are available in two endstations.

Besides classical crystal structure determination it is possible to investigate phase transitions, disordered an modulated structures at ambient and non-ambient conditions and dynamics

Keywords: Chemical crystallography, synchrotron radiation

MS23- Advances in electron crystallography methods

Chairs: Dr. Mariana Klementova, Dr. Enrico Mugaioli

MS23-P12

Experimental and computational reduction of dynamical electron scattering allows visualizing individual hydrogen atoms

Max Clabbers¹, Tim Gruene², Eric van Genderen², Jan Pieter Abrahams²

1. C-CINA, Biozentrum, University of Basel, Basel, Switzerland

2. Paul Scherrer Institut (PSI), Villigen, Switzerland

email: clabbersm@gmail.com

Electron crystallography allows structure solution of beam-sensitive organic pharmaceuticals and macromolecules when only nanometre-sized crystals are available. Compared to X-rays, electron diffraction faces a crucial challenge: dynamical electron scattering compromises structure solution and its effects can only be modelled in specific cases. Dynamical scattering can be reduced experimentally by decreasing crystal size - but not without a penalty, as it also reduces the overall diffracting intensity. To boost the very weak diffraction data, the crystals were cryo-cooled and we employed a fast and highly sensitive hybrid pixel detector. Here we show that nanometre-sized crystals from organic pharmaceuticals allow visualization and unconstrained positional refinement of the hydrogen atoms, even whilst ignoring the effects of dynamical scattering during refinement. Furthermore, we introduce a general likelihood-based computational approach for further reducing the adverse effects of dynamic scattering, which significantly improved model accuracy - even for protein crystal data at substantially lower resolution.

Keywords: electron diffraction, hydrogen atoms, dynamical scattering
MS36 Structure and function in inorganic and coordination complexes

Chairs: Dr. Attila Benyei, Prof. Alessandra Crispini

MS36-O1

Selection of tautomers in the solid state driven by metals and other inorganic components

Roberto Centore¹

1. Department of Chemical Sciences, University of Naples Federico II, Naples, Italy

email: roberto.centore@unina.it

Tautomers are structural isomers in ready equilibrium between each other. In the most common case of tautomerism, i. e. prototropism, tautomers differ for the position of hydrogen atoms inside the molecule and for the distribution of π electrons.

In a certain sense, tautomers can be considered as "living molecules", because of the thermodynamic equilibrium they undergo. In fact, the relative amounts of the forms can be altered by physical or chemical factors (temperature, solvent, pH, mechanochemical processes etc.), and so a tautomeric system can face a change in ambient conditions by favouring one form over the others. This responsiveness of tautomeric systems is appealing for the development of smart materials.

The dynamic equilibrium between the different tautomeric forms of a compound in solution can lead to different outcomes for the crystallization from solution: crystallization of only one tautomeric form (likely, but not necessarily, the most stable in solution), co-crystallization of different tautomers in the same lattice, concomitant formation of crystals of different tautomeric forms. Altogether, crystallization of different tautomers of the same compound is a rare occurrence and only around 0.5 % of molecules able to tautomerize and archived in the Cambridge Structural Database are actually observed in different tautomeric forms in the solid state.1 This can be related with the fact that for many potentially tautomeric systems, the energy difference between the tautomers is high (>3 kcal/mol) and so only one form is prevailing by far in solution and found in the crystals.

In the present communication, we will discuss examples of tautomeric systems for which, out of many tautomers present in solution, the selective precipitation of only one tautomer is achieved in the solid state. The selectivity is provided by metal complexation2 or by formation of salts with suitable inorganic counterions.3 Examples include ring to open-chain tautomerization in dithiocarbazate ligands and tautomers of neutral and singly protonated N-rich fusedring triazolotriazoles.



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82, 5155-5161.

Keywords: tautomer, metal coordination, salt

MS36-P36

Reactions of C-halogen Bond Activation Mediated by a Rhodium POP Complex

Laura Andrea de las Heras Martín¹, Sheila G. Curto¹, Miguel A. Esteruelas¹, Montserrat Oliván¹, Enrique Oñate¹

 Departamento de Química Inorgánica – Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Centro de Innovación en Química Avanzada (ORFEO-CINQA), Universidad de Zaragoza – CSIC, 50009, Zaragoza, Spain

email: laandelash@gmail.com

The reactions of C-halogen bond activation are fundamental steps in organic transformations mediated by transition metal complexes, such as cross-coupling reactions, las well as in the chemical destruction of halogen-containing organic pollutants, among other processes.

Recently we have shown that the complex RhH{xant(PiPr2)2} (xant(PiPr2)2= 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene) reacts with fluoroarenes to give products resulting from processes of C-H bond activations,2 while in the case of chloroarenes the C-Cl bond activation takes place (Figure 1).3 In the present contribution, we will show the preliminary results of the reactivity of the related complex RhCl{xant(PiPr2)2} towards halogenated hydrocarbons. The X-ray diffraction analysis of the products obtained have helped us confirm its reactivity.

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Keywords: POP-Rhodium Complex, C-Cl bond activation, Cross-couplinga

MS36-P37

Solid State Thermochromism in an Octahedral Co(ii) Complex Studied by X-Ray Powder Diffraction

Rosario Pedrero Marín¹, Fernando José Barros-García¹, Álvaro Bernalte-García¹, Francisco Luna-Giles¹

1. Organic and Inorganic Chemistry Department. University of Extremadura, Badajoz, Spain

email: rospema@unex.es

Thermochromism is the phenomenom known as the reversible change in the colour of a compound when it is heated or cooled [1]. This process can take place over a wide (continuous thermochromism) or a narrow (discontinuous thermochromism) range of temperature. The latter, typical of inorganic substances, may be associated to a structural phase transition [2].

In the present work, we have studied the colour change in the pink octahedral cobalt (II) complex [CoCl2(PyTn)]·2H2O [PyTn: 2-(pyrazol-1-yl)-2-thiazoline] [3] in the solid phase over a temperature range from 30°C to 160°C by means of powder X-ray diffraction. This compound, previously studied in solution, transforms into the blue dinuclear asymmetrical complex $[CoCl2(\mu-Cl)2Co(PyTn)2]$. The thermochromic transition temperature is considerably higher in the solid state than in solution, as it was expected.

Colour transformation was monitored by means of in-situ X-ray powder thermodiffraction with the aim of discovering reaction intermediates. The X-ray experiment was carried out on a Bruker D8 Advance powder diffractometer equipped with a temperature chamber, using CuKal radiation. Measurements were made in the 10-30°20 range and collected at temperature intervals of 5°C.

Reaction product was identified by comparing the measured patterns to the simulated one for known single crystal structure using Mercury CSD software. In additon, TG-DTG curves were obtained in a dynamic air atmosphere in the same temperature range, as well as a DSC curve. From these, it can be concluded that only the two crystallization water molecules are released, keeping the compound its integrity

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Keywords: thermochromism, X-ray powder thermodiffraction, cobalt (II) complex