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Polypyridyl Ligands: Synthesis, Characterization and Biological Applications; Olufunso O. Abosede
Effect of structural and microstructural features on the performance of CoMn$_2$O$_4$ as anode material in lithium ion batteries

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Cobalt-dimanganate samples were prepared by the precipitation route at RT. Additionally, samples were thermally treated at T=300-500 °C. Structural investigation using XRPD and Raman spectroscopy have been carried out in order to correlate specific structural features with preparation conditions and furthermore with electrochemical properties. Changes in unit-cell as function of temperature were calculated; observed decrease is inconsistent with simple spinel-type exchange of Co$^{2+}$ by Mn$^{3+}$ on the tetrahedral site, and vice versa on the octahedral site. Based on the Raman spectroscopy an alternative structural model: $^{IV}[Co^{2+}]_{1-x}Mn^{2+}_{x}$ $^{VI}[Co^{3+}]_{x}Mn^{3+}_{2-x}$O$_4$ has been proposed. Rietveld refinement showed increase of M-O distances within tetrahedra, caused by thermally enhanced substitution of Co$^{2+}$ by larger Mn$^{2+}$ cations at A-site. Consequently, octahedral B-site becomes partially occupied by Co$^{3+}$ on the account of the transferred Mn cations.

In all samples, initial capacity drops as commonly observed in high capacity metal oxide materials. However, after a certain number of cycles specific capacity increases again. Among all samples, thermally treated from 100-500 °C, highest specific capacities are observed for sample thermally treated at highest temperature (500 °C) despite its large particle size. Thus, contrary to the common assumption that nanostructuring of the anode material improves the battery performance, samples with the largest particle sizes exhibit excellent performance with a capacity retention of 104% after 1000 cycles (compared to the 2nd cycle).1

1. M. Bijelić, X. Liu, Q. Sun, A. Djurišić, M. Xie, A. M. C. Ng, C. Suchomski, I. Djerdj, Ž. Skoko & J. Popović, Long cycle life of CoMn$_2$O$_4$ lithium ion battery anodes with high crystallinity J. Mater. Chem. A, 2015, 3, 14759
One molecule, four colours: remarkable behaviour of 2,3-thieno(bis)imide based molecule which presents four different polymorphs with dramatic different emissions

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2,3-Thieno(bis)imide (TBI) based materials are emerging as valuable molecular materials for application in organic electronics thanks to their ambipolar charge transport properties combined to tunable electroluminescence. This new class of materials is being tested as active layer in thin films organic devices, such as ambipolar light emitting transistors (OLETs), field-effect transistors (OFETs) and both as donor and acceptors in photovoltaic cells (OPV). These molecules often present different crystalline modifications which show different photophysical properties. One of these molecules, named NTA¹, shows a strong tendency to form different polymorphs. Until now we have observed at least four different crystalline phases, each one characterized by a particular colour, emission under UV light and crystals morphology (Figure 1). Form II and Form III shows green and red emission respectively and their structure was determined by single crystal x-rays diffraction. Form I and form IV shows yellow and orange emission, and their powder pattern are clearly different form the previous form. Phase transition from I → IV has been observed in variable temperature XRPD collected at PSI. The main interaction that drives the crystallization of Form II and III is the π-stacking between the aromatic cores of the molecules, forming channels possibly suitable for the charge transport. The form III seems to be the most appropriate for the charge transport due to the packing of the molecules that form columnar stack linked together through π-π interaction. The thermal behaviour was also investigated with hot-stage microscopy and DSC; it was observed that the forms I, II and III, obtained by different types of crystallization, convert in form IV upon thermal annealing; the solid-state transition is clearly visible due to a variation in the color of the emission under UV light.

Figure 1: scheme of polymorphism of NTA

Crystal engineering of new crystal forms of venlafaxine

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Solid state chemistry and powder diffraction methods have been attracting the attention of many researchers and industries in the pharmaceutical field, in which the aspect of discovery and development of new solid forms of APIs is particularly important. Co-crystallization can provide a different strategy to obtain new active pharmaceutical ingredients by altering the chemical and physical properties (solubility, dissolution rate, thermal stability, etc) of molecular solid forms without altering the chemical entity of the API.

The goal of this project has been the preparation of multicomponent crystals, in our case molecular salts, between the antidepressant venlafaxine and Pharmacopeia accepted acids, their solid-state characterization by X-ray diffraction methods, and the optimization of the solid-state products for tableting and dissolution properties analysis. The mechanochemical as well as the solution reaction between venlafaxine and oxalic, fumaric, coumaric, ferulic and salicylic acids leads to protonation of the amino group and formation of the corresponding 1:1 molecular salts. The use of mechanochemistry is an attractive route 1 to produce new crystal forms of APIs, which may help in reducing problems related to the use of large amounts of solvents. 2

In the solid state chemistry there are often problems due to: i) crystallization of multicomponent crystals, ii) products obtained by mechanochemistry. In cases in which suitable crystals for single crystal X-ray diffraction are not obtained, powder diffraction is more than a simple finger-print characterization technique, but can represent the solution for these kind of problems.

Figure 1. Crystal structure of the antidepressant venlafaxine.

Optimizing physicochemical properties of a natural antioxidant and geroprotector L-carnosine

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The issue of “Healthy Ageing” has become a significant challenge because of the continuous population ageing, and increasing life expectancy is accompanied by a higher danger of development of age-associated diseases. For this reason, the increasing interest in natural antioxidants is not surprising. The antioxidant L-carnosine, a dipeptide of amino acids β-alanine and L-histidine, is being investigated for its properties as geroprotector, as it seems to have an effect in reducing the risk of development of ageing-related diseases. Nowadays design, formulation and characterization of multiple crystal forms (salts, co-crystals, solvates and polymorphs) are widely studied areas in the broad field of crystal engineering, as multiple crystal forms of molecules of pharmaceutical interest represent a way to modify/improve physicochemical properties and to satisfy the criteria of patentability, i.e. novelty, nonobviousness and utility.

A range of organic acids were tested as possible co-formers in the reaction with L-carnosine. Nine new molecular salts were thus prepared by reaction with GRAS organic acids. Obtaining the molecular salts in a crystalline form turned out to be quite a challenge; they were then characterized via both diffraction and thermal methods. The structures of 6 of them could be determined by using X-ray Powder Diffraction (XRPD).
Improvement of model quality by rejection of non-isomorphous frames using \( \text{CC}_{1/2} \) and the data processing user interface XDSGUI

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XDSGUI is a lightweight GUI (graphical user interface) for XDS that supports both novice and experienced users to obtain high-quality data processing results. The program enables XDS data processing without the command-line and supplies additional graphical information, in a user-modifiable way. Graphical evaluation with XDSGUI of SBDG reference data sets (SNX17 FERM domain, 5 partial merged data sets)\(^1\) demonstrates that applying the \( \Delta \text{CC}_{1/2} \) method\(^2\) to single frames of one data set easily detects single non-isomorphous frames, which can occur because of radiation damage or experimental setup related errors, e.g. Rejection of these non-isomorphous frames for every partial data set and reprocessing with XDSGUI and XSCALE showed improved data statistics such as increased \( \text{CC}_{1/2} \)\(^3\), and increased internal correlation of the merged data sets. Moreover, comparison with the previously published model\(^4\) by the correlation coefficient of calculated (\( \text{F}_{\text{calc}} \)) and observed intensities (\( \text{F}_{\text{obs}} \)) showed an improved correlation after rejection of the identified non-isomorphous frames. \( \text{CC}_{1/2} \) therefore correctly predicts non-isomorphism and the agreement of data and model.


\(^3\) Karplus P. A., Diederichs K. (2012). *Science* 336, 1030-1.033

Deprotonation induced assembly of bulky silanetriols

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The formation and structural characterization of the first dilithium salt of a tetrahydroxydisiloxane, [DmpSi(OH)OLi]2O (3), was recently reported (Dmp = 2,6-dimesitylphenyl).1 The solid state structure reveals the presence of a dimeric motif where two disiloxane units are linked by coordinating lithium atoms which differs from those found for the sodium1 (4) and potassium4 analogs. The arrangement imposed by the cluster formation leads to diastereomeric silicon atoms exhibiting (R,S) configuration in the solid state. In addition, the intermediates of the reaction, monolithiated and dilithiated silanetriols could be identified.

The hydrogen bond acceptor guided self-assembly of silanetriols with 4,4'-bipyridine leads to infinite columns of cofacially arranged π-stacks as evidenced by X-ray data.2 Variation of the silanetriol (DMP or t-Bu) reveals a subtle balance between hydrogen bonding and π-interactions which by proper choice of the substituent may foster either dominant hydrogen bonding or dominant π-interaction.

The authors would like to thank the PhD networks SHINE (EU-ITN) and FreCheMaterie (Austrian BMWF) for financial support. We also are grateful to the EU-COST network CM1302 “Smart Inorganic Polymers” (SIPs).

Figure 1. Preparation of 3, 4 and 5.

Computational study of the substrate specificity of monoamine oxidase B

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Histamine plays an important role in the human body and is involved in more than twenty different physiological processes. Due to histamine potent physiological activity, its degradation has to be carefully regulated to avoid adverse reactions. The major routes of histamine inactivation in mammals include monoamine oxidase B (MAO B) and diamine oxidase (DAO) enzymes. The fact that MAO B metabolizes only N-methylhistamine while DAO prefers histamine1-2, pinpoints their remarkable selectivity towards two compounds that differ only in one methyl group. The mechanism of enzyme catalysis and specificity are usually elucidated from the differences in mechanistic aspects of enzymatic reactions for each possible substrate, which provide unambiguous quantitative information about the thermodynamics and the kinetics of reaction pathways. Unfortunately, mechanistic studies are not always experimentally approachable. Therefore, we utilized a combination of molecular dynamics (MD) simulations, MM-PBSA binding free energy calculations and quantum mechanical cluster approach to address substrate specificity and mechanism of MAO B catalysis. We have identified favourable hydrophobic interactions between methyl group of the N-methylhistamine substrate and the hydrophobic side chains of the enzyme binding site that keep substrate anchored and properly oriented for the enzymatic reaction. Since histamine is deprived of methyl group it cannot be properly anchored and rotates within the active site, which results in non-productive orientation for the reaction. Quantum-chemical mechanistic analysis within the cluster model of the enzyme revealed higher activation parameters for histamine relative to its N-methyl counterpart, thus aiding in rationalizing the mentioned selectivity. Inspection of the calculated free-energy profiles (Figure 1.) convincingly shows that MAO B selectivity for the N-methylhistamine over histamine is a result of two synergistic effects: lower activation barrier and more favourable reaction thermodynamics. Moreover, reaction pathway obtained from QM calculations is consistent with recently proposed hydride mechanism of MAO B mechanism of catalysis3-4.

Figure 1. Free-energy profiles for the MAO B catalyzed degradation of N-methylhistamine (left) and histamine (right)

The first crystal structure of plant aminoacyl-tRNA synthetase: seryl-tRNA synthetase from *Arabidopsis thaliana*

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Seryl-tRNA synthetase (SerRS) plays an essential role in the translation process by covalent attachment of serine to its cognate tRNA<sup>Ser</sup>. Most SerRS enzymes belong to the so called bacterial type that is found in most archa, bacteria and eukaryotes. A small number of enzymes found in methanogenic archa show structural and mechanistic differences and can be classified as methanogenic type<sup>1</sup>. Moreover, higher eukaryotic SerRS, like human SerRS, possesses two types of additional insertions: Insertion I (G75-N97) and Insertion II (K253-N261) located in the tRNA binding domain and in the catalytic core, respectively<sup>2</sup>. Until now the crystal structure of human SerRS, as well as of several prokaryotic systems and lower eukaryotes, have been studied by X-ray crystallography while no crystallographic structure of any plant SerRS is known to date.

In order to clarify the structural and functional properties of plant SerRS (pSerRS) we performed cloning, purification, crystallization and X-ray analysis. Plate-like crystals were prepared by the sitting drop vapor diffusion method using an automated crystallization platform (Oryx 8 robot). Diffraction data were measured at the XRD1 beamline (Elettra, Trieste, Italy) and were collected to the resolution of 2.8 Å. The crystals belong to the monoclinic space group *C2*. The structure of pSerRS was solved by the molecular replacement method while further model building and refinement is in progress.

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RNA-binding properties of the archaeal Sm-like protein from *Haloarcula marismortui*

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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. Bacterial Lsm protein Hfq act as an RNA chaperone to facilitate interaction between regulatory RNA and mRNA, eukaryotic Sm/Lsm proteins are mainly scaffold proteins of spliceosomes and telomerases, but the role of Lsm proteins in archaea is explored poorly.

In our work, the RNA-binding ability of archaeal Sm-like protein from *Haloarcula marismortui* has been studied by X-ray crystallography and by fluorescent measurements. Earlier we have demonstrated that it is possible to determine single-stranded RNA-binding sites on the protein surface using a soaking procedure followed by structure determination of the obtained nucleotide–protein complexes. The SmAP *H. marismortui* protein was isolated and purified. Crystals of the protein and its complexes with ribonucleotides were obtained. Using our crystallographic approach, we have determined potential single-stranded RNA-binding sites on the protein surface. In addition, AMP affinity to the protein has been determined by measuring of fluorescence changes during titration of the AMP-MANT solution by the protein.

*This work was supported by Russian Scientific Foundation (project 14-14-00496).*

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Polymorphism of novel double complex salt
\[ \text{[CoC}_2\text{O}_4(\text{NH}_3)_4]\text{[Fe(C}_2\text{O}_4)_2(\text{OH})_2] \cdot 2\text{H}_2\text{O} \]

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Double complex salts are class of chemical compounds in which both cation and anion are complexes with their own electric charge. One of many applications of these compounds is as precursors in preparation of various bimetallic oxides which can be used as catalizators due to their distinctive structures and properties.\(^1\) It has been known that their thermal decomposition, which can be accompanied with reduction, results in homogenous mixture of metals and/or their oxides.\(^2\)

Novel double complex salt described with formula \[ \text{[CoC}_2\text{O}_4(\text{NH}_3)_4]\text{[Fe(C}_2\text{O}_4)_2(\text{OH})_2] \cdot 2\text{H}_2\text{O} \] was prepared by reaction of \[ \text{[CoC}_2\text{O}_4(\text{NH}_3)_4]\text{NO}_3 \cdot \text{H}_2\text{O} \] with \[ \text{K}_3[\text{Fe(C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O} \] under various reaction conditions, molar ratios and concentrations of reactants. Depending on the reaction conditions, it was possible to isolate two polymorphs. Molecular and crystal structure of both polymorphs was determined using single-crystal X-ray diffraction. Both polymorphs were further characterized by means of IR-spectroscopy, thermal analysis and powder X-ray diffraction method.

Diffraction effects of nanostructured aluminum oxides

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Nanocrystalline materials are of considerable interest because particle morphology to affect physicochemical properties. Investigation of the relationship between properties, atomic structure and nanostructure of materials is an actual problem.

So various nanostructures of aluminum oxides can be obtained depending on the preparation conditions. The difference between morphology of the structures is revealed by microscopy and diffraction investigations [1]. This can appear as anisotropic broadening of the diffraction peaks, redistribution of the intensities or appearance of diffuse scattering.

Interpretation of nanostructures involves identifying specific shape/size of primary nanocrystallites and identification their type of coherent ordering. The objective of this work is the illustration of possibilities of the diffraction method for research of nanostructured systems.

The method based on the Debye equation [2] is known in the literature as Debye Function Analysis (DFA) [3]. It is full-profile method which is applicable for any an arbitrary atoms collection, and therefore can be used for crystalline materials or nano-structured objects. For this purposes the approaches are developed based on previously submitted program [4]. It is public-domain software and available on the website: www.sourceforge.net/projects/dianna.

This work is supported by Russian Science Foundation project N 14-23-00037.

Lithium localisation and quantification by quantitative electron diffraction tomography in new AVPO₄F (A = Li, K) cathode materials for high power rechargeable batteries

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We synthesized new Li₀.₇₀K₀.₁₂VPO₄F fluorophosphate using ion exchange. This method allows obtaining Li cathode materials that are isostructural to Na or K analogues and that cannot be obtained by direct synthesis due to thermodynamic reasons. In such structures, the alkali metal resides in the channels of the framework and can be easily deintercalated upon charge thereafter Li can be inserted upon discharge.

The initial KVPO₄F fluorophosphate has a KTiOPO₄ type structure, with a 3D system of continuous spatial cavities and two potassium positions [1]. In order to obtain the Li analogue, potassium is extracted by charging up to 5.0 V vs Li/Li⁺.

The crystal structure was determined by selected area electron diffraction and quantitative electron diffraction tomography (EDT), which can obtain diffraction data from submicron crystals (100-200 nm). This allowed us to solve and refine the structure of the charged and discharged materials, whereas bulk diffraction methods are hindered by the presence of the obligatory extra phases, such as carbon, which needed for a functioning battery.

Potassium was not fully deintercalated (17% left) and it remains in the K2 site, whereas the K1 site is not occupied. At the same time, the structure changes from noncentrosymmetric (Pna2₁) to centrosymmetric (Pnan).

After lithiation, the K2 site is shared by K and Li but K1 site is still empty. Li is found in a new Li3 position that was located by the use of difference Fourier maps calculated from EDT data. This Li3 has [4 + 2] coordination with four short 1.99−2.14 Å Li3−O bonds. Both Li sites reside in the channels along the b axis, which results in a row of Li atoms with alternating occupancy. The Li3 position can accept only 0.5 Li and it is fully occupied. The rest 0.2 Li is present in the K2 site. It can be concluded that Li prefers to reside in the site with the close oxygen environment instead of the K1 and K2 sites that are surrounded by oxygen and fluorine at a 2.7−2.9 Å distance.

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Exploiting IRMOF-9 porosity as nanoconfined environment for the synthesis of Si, Ti and Zr oxide aggregates

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The ordered porosity of Metal Organic Frameworks is commonly acknowledged as the most important feature in making these crystalline solids very popular among manifold classes of functional materials. Their usage as trapping host towards several classes of guest species is indeed often the main topic in the research field concerning their applications. Furthermore, the crystallinity of these solids can in principle allow structural information to be acquired on the situation of the trapped species, if with any degree of order, by means of X-ray analyses.

In the present research, IRMOF-9, a Zinc and biphenyl-4,4'-dicarboxylate based MOF, has been used to trap molecular precursors for silica, zirconia and titania particles, the perspective being to trigger the hydrolysis of precursor and synthesize the final material in a nanoconfined environment. While the structural characterization of the guests and of their final products seemed a hard task to achieve due to the loss of a short-range order, their presence seem to influence the behaviour of the MOF with temperature changings.

For example, crystals soaked in Ti isopropoxyde and then exposed to the air for a few minutes seem to retain their symmetry and structural properties after cooling it down to 100K, whereas specimens soaked in tetraethyl orthosilicate (TEOS) exhibit, with the temperature drop, a symmetry breakage typical of the starting solid (Figure 1). This is reasonably due to the formation in the MOF cavities of a structured titania aggregate which prevent the conformational freedom of the crystals. Further studies are needed to define the nature of such phases and their structural features.

Figure 1. Different structural behaviour of the IRMOF-9 after soaking in two different liquid precursors (TEOS and Ti isopropoxyde), as observed by collecting the single crystal XRD data at 100K.

Bacteroides thetaiotaomicron dipeptidyl peptidase III complexes with synthetic substrates

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Dipeptidyl peptidase III isolated from Bacteroides thetaiotaomicron is a two-domain zinc exopeptidase from the M49 family. Members of this family, characterized by HEXXGH and EEXR(K)AE(D) motifs, cleave dipeptidyl residues from the N-terminus of their substrates. This conserved region contains two His residues that coordinate the Zn ion along with Glu449 and Glu476. The BtDPP3 crystal structure1 shows two domains separated by a cleft, strongly resembling the human DPP3 despite the low sequence identity (~23%).

In this work we performed docking of synthetic substrates Arg-Arg-2-naphtylamide and Lys-Ala-2-naphtylamide in the wild-type DPPIII and its C450S mutant in order to understand enzyme-ligand interactions. The starting structures were prepared from the human DPPIII-RRNA complex used in previous studies2. Complex simulations were performed over the course of 200 ns using ff12sb and ff14sb force fields. These force fields were selected based on their good performance in conformational studies of both human and bacterial DPPIII. Special emphasis has been placed on the zinc ion coordination flexibility, since the existing data for human DPP3 suggests the high plasticity of the Zn$^{2+}$ coordination3.

Our results are in qualitative agreement with available kinetic data4 and represent a good starting point for further QM/MM studies necessary to elucidate the mechanism of the bacterial DPPIII.

1. Sabljić, I., internal correspondence
The active site structure of manganese-containing *Brassica rapa* auxin-amidohydrolase BrILL2

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Auxin-amidohydrolase from *Brassica rapa* (*Br*), BrILL2, belongs to the M20D metallopeptidase subfamily, related to the amidohydrolase superfamily (M20) of enzymes which hydrolyze a number of different substrates, including amino acids, sugars, nucleic acids, and organophosphate esters.\(^1\) BrILL2 is catalytically the most efficient auxin-amidohydrolase from *Br*, playing a key role in homeostasis of the plant hormone auxin in a way to hydrolases amino acid conjugates (AACs) of auxins (IAA, IBA, IPA). A large concentration of free auxins, of which the most common is indole-3-acetic acid (IAA), is toxic for plants, so only about 5% of the total concentration of auxin molecules in plants is in the free (active) form, while the rest is stored in inactive forms, mostly as amino acid and sugar conjugates.\(^2\) In order to hydrolyze the amide bond of amino acid conjugated auxins (inactive, storage forms), and release the free auxin, BrILL needs manganese.\(^3\) The aim of our research was to determine number of the manganese ions, Mn\(^{2+}\), in the enzyme active site, and the influence of Cys to Ser mutations on the protein structure and activity. In order to fulfil this aim we conducted an interdisciplinary study combining different experimental and computational approaches: biochemical, spectroscopic, calorimetric and computational.

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Hybrid Perovskite Solar Cells: Active layer deposition methods and parameter influences

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In this century the population of the world has risen by 21%. This coupled with the increasing energy consummation per capita has determined an increase of green house emissions caused by conventional energy sources. One solution to this ever growing problem is the use of environmentally friendly energy sources like solar cells. Research in this field has been going on for more than 35 years, new types of photovoltaic structures been developed in a continuous effort to improve efficiently and cost.

Hybrid perovskite solar cells are a type of photovoltaic devices that have gathered a lot of attention in recent years, having attained a maximum efficiency of 20.8% in only 4 years.¹ An halide hybrid perovskite with the general formula MPbX₃ (where M is a organic ion and X is I, Br or Cl) is the active material of the device. Its excellent light absorbing properties and the possibility of synthesis by wet chemistry makes this type of material very interesting for high efficiency – low cost solutions. CH₃NH₂PbI₃ and CH₃NH₂PbI₃₋ₓClₓ are the most used perovskites because of their band-gap and electron-hole diffusion lengths², a one-step or two-step method being employed for the deposition of the active layer.³⁵ The key parameters and vulnerabilities of each method will be discussed in this study, additional post and during deposition treatments being also addressed. Because of the degradation of this type of solar cell a highlight of the possible mechanisms, sites and solutions will be produced.

⁴ Im, J.H., Kim, H.S. & Park, N.G. (2014). APL Mat. 2(8), pp. -
Structure features of \( (R_{0.95}Bi_{0.05})Fe_3(BO_3)_4 \) \( (R = \text{Gd, Y}) \) single crystals in the temperature range 30–295 K

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Rare-earth iron borates \( RFe_3(BO_3)_4 \) \( (R=\text{Y, REE}) \) attract considerable attention due to their structural and magnetic behavior.1 Iron borates reveal a cascade of phase transitions: structural, magnetic, spin-reorientation.2–5 Variety of their properties is caused by the presence of two magnetic subsystems: Fe ions and rare earth ions. The main structure feature of these compounds is the presence of helical chains along \( c \) axis formed by Fe atoms. Structural phase transitions occur in some of them at 88–450 K reducing \( R32 \) symmetry to \( P3_121 \). Many questions concerning the structure-properties relationships of \( RFe_3(BO_3)_4 \) are still not clarified.

The low-temperature crystal structure, lattice parameters and atomic positions for many crystals of this family and also the high-temperature structure for some of them has not been studied yet.

In the present work the structures of \( (R_{0.95}Bi_{0.05})Fe_3(BO_3)_4 \) \( (R = \text{Gd, Y}) \) single crystals have been studied. The Bi atoms were detected in the structures by energy-dispersive X-ray analysis. Unit cell parameters have been measured over the 295–30 K range using the Huber-5042 diffractometer equipped with point detector and a Displex DE-202 helium cryostat (APD Cryogenics). With temperature decreasing the unit-cell parameters \( a \) and \( b \) of \( Gd_{0.95}Bi_{0.05}Fe_3(BO_3)_4 \) preserve their values until \( T_{\text{SN}} = 155 \text{ K} \) and then the values reduce abruptly indicating the structural transition \( R32 \rightarrow P3_121 \). After that the values decrease with temperature decreasing from 155K to 30K. There is no phase transition for \( Y_{0.95}Bi_{0.05}Fe_3(BO_3)_4 \) \( (P3_121 \) sp.gr.) in this temperature range. The \( c \) parameter decreases for both crystals from 295 K to 80 K and then its value increases with a smooth decrease of \( a, b \) parameters and volume. X-ray diffraction measurements at 293 K, 90 K and 30 K were carried out using the Xcalibur CCD (Rigaku Oxford Diffraction) with CryoJetHT (Oxford Instruments) open-flow cooler and Huber diffractometers. The calibration of the CryoJetHT cooler was performed. The crystal structures have been refined using the JANA20066 and ASTRA7 programs. At room temperature the \( Gd_{0.95}Bi_{0.05}Fe_3(BO_3)_4 \) crystals have \( R32 \) sp.gr., the \( Y_{0.95}Bi_{0.05}Fe_3(BO_3)_4 \) \( \rightarrow P3_121 \) sp.gr. At 90K and 30K both compounds belongs to \( P3_121 \) sp.gr. There is one type of Fe atoms in \( R32 \) whereas there are two independent positions in \( P3_121 \). Upon lowering the temperature from 293 to 30 K the distortions of the \( R(BO)_6 \), \( \text{FeO}_6 \) and \( \text{B}(2)\text{O}_3 \) coordination polyhedra are observed for both crystals. The Fe1–Fe1 distances in the helical chains along \( c \) axis decrease, the Fe2–Fe2 distances increase, the angles Fe–O–Fe change nonuniformly. The shortest distances between 3 chains in \( ab \) plane become reduced, the most distant distances expand. The existence of two Fe crystallographic positions might lead to emergence of two magnetic Fe positions below the Neel temperature. The distortions in the crystal structure can affect the magnetic properties.

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A new route to NaOsO₃ post-perovskite

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The study of electronic and magnetic responses of 5d compounds is at the centre of a considerable research effort due to their fascinating properties which make them suitable for spintronics and other advanced electronic technologies. In particular, several Na-Os oxides systems (e.g. Na₂OsO₄, Na₃OsO₆, Na₅OsO₆) have been extensively studied, while others, such as NaOsO₃, have been only briefly described. All these compounds belong to the K₂Sb₂O₆-type family and combine certain structural motifs (cP, (Pn̅3) and (Im̅3) symmetries) with great chemical variability. They are therefore ideal to explore new synthetic protocols that can exploit changes in oxidation state and bulk chemistry to produce novel phases. The recent identification of a perovskite phase in NaOsO₃ has generated quite some interest, as it displays a continuous metal-insulator transition driven by 3D antiferromagnetic order. However, the synthesis is rather complex and should cope with the requirements of increasing the oxidation state of osmium from IV to V, avoiding the production of toxic OsO₄ and being held in a generally reducing high pressure assembly.

In this work, the perovskite-phase (pv) of NaOsO₃ was synthesized under high-pressure and high-temperature. The formation of post-perovskite phase (ppv) has been investigated in situ using large-volume multi-anvil press installed at the ID06LVP beam-line, ESRF. The pv to ppv transition occurs at 16.35 GPa and 1135 K (see figure). Quenched to ambient conditions, the ppv's lattice dimensions can be indexed and refined in the Cmcm space group with \(a = 2.8323(3), b = 10.6927(14), c = 7.3345(7) \text{ Å}, \) and \(V = 222.12(4) \text{ Å}^3\).

Two different synthetic routes were explored.¹ Firstly, ppv NaOsO₃ was produced from the GdFeO₃-type pv phase of NaOsO₃, even though all the structural criteria commonly used to predict such a transition were not fulfilled (values of tilting angle, tolerance factor and polyhedral volume ratio were well outside established boundaries).² The second route includes a production of the ppv phase from an assemblage which did not contain any perovskite-structured compound. Indeed, the growth of pv as a precursor or indicator to ppv appeared counterproductive, requiring a pressure 10 GPa higher to initiate transformation.

This work suggests that ppv can be obtained in other compounds and chemistries where generalized rules based on pv may not apply, or where no pv is known. Rather, pv formation may even mask and hinder other less extreme chemical pathways to ppv phases.

Syntheses and crystallographical study of 2-acetylpyridine-aminoguanidine and its copper(II) complexes

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The survey of Schiff bases of non-substituted and substituted aminoguanidine in Cambridge Structural database\(^1\) revealed 77 structures with 54 different carbonyl\(^1\) compounds. However, the number of structurally characterized complexes with these Schiff bases is still small. The most numerous are complexes of copper(II) with pyridoxilidene aminoguanidine\(^2\) and salicylidene aminoguanidine.\(^3\)

Having in mind the recognized biological importance of aminoguanidine and its Schiff bases as well as their interesting coordination behavior we found it important to examine the syntheses and characteristics of copper(II) complexes with the Schiff base of aminoguanidine and 2-acetylpyridine.

Dichloride and sulfate salts of the ligand 2-acetylpyridine-aminoguanidine were isolated in the form of single crystals, thus the first structural data on this ligand are described. The reaction of warm aqueous solution of the appropriate Cu(II) salt and methanolic solution of dichloride ligand in molar ratio 1:1 resulted in formation of green single crystals of the complexes. Ligands and the complexes are characterized by IR spectra, conductometric measurements and X-ray analysis. In these complexes chelate ligand is coordinated in its neutral form in a tridentate \(N_3\)-coordination mode, via pyridine, azomethine and imino nitrogen of aminoguanidine fragment. Cu(II) is situated in a moderately or severely distorted square-pyramidal surroundings (the distortion from the ideal geometry is described by \(\tau_5\) parameter\(^4\)). The compound [CuLCl\(_2\)] (Fig. a) was isolated in two polymorphic forms, both in monoclinic system and \(P2_1/c\) space group. However, their crystal structures greatly differ. The asymmetric unit of the other complex (Fig. b) contains two [CuL(Cl)MeOH]\(^+\) cations and two NO\(_3^-\) anions arranged in a peculiar way so that [CuL(Cl)MeOH]NO\(_3^−\) subunits are pseudo-symmetrically related by non-crystallographic two-fold rotation axis. Common fragments encountered in the structures were compared by r.m.s. overlay calculations as well as half-normal probability plots.

Fig. Molecular structures of the complexes [CuLCl\(_2\)] (a) and [CuL(Cl)MeOH]NO\(_3^−\) (b).

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Structural studies of dipeptidyl peptidase III from *Caldithrix abyssi*

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Dipeptidyl peptidase III (DPP III), a zinc peptidase of the M49 family, is a cytosolic enzyme widely distributed among eukaryotic and prokaryotic organisms. Currently, three crystal structures are available in the protein data bank (PDB): the human enzyme, free and as a complex with tynorphin4, as well as yeast enzyme2. The binding of inhibitors induces a large domain motion from so called open to closed conformation. Up to now, there is no structural information on prokaryotic DPP III.

We have been studying DPP III from the bacterium *Caldithrix abyssi* (Ca), which inhabits hydrothermal vents. The gene encoding CaDPPIII was heterologously expressed in *Escherichia coli* and the generated protein was purified using affinity and size exclusion chromatography. Using diverse crystallization screens, first crystals were obtained and crystallisation conditions were optimised. A dataset was collected up to 2.3 Å at the Elettra Sincrotrone Trieste, Italy at a wavelength for anomalous scattering of the zinc atom (1.27 Å). Unfortunately, scattering was too weak for the structure to be solved using the single-wavelength anomalous dispersion of the zinc atom. Also, all efforts to solve the structure using molecular replacement were unsuccessful. Therefore, selenomethionine-labelled protein was prepared, and crystals were grown under similar conditions as for wild-type protein. The crystal structure was solved using multi-wavelength anomalous dispersion of selenium atoms. CaDPP III crystallized in the space group *P* 212121 with one molecule in the asymmetric unit. The overall topology of CaDPPIII is very similar to the fold for other members of the M49 family with two structural domains separated by a cleft. However, in comparison to the structure of the yeast and human enzyme, CaDPP III adopts a conformation between the (fully) open and closed structure (Fig. 1). As CaDPP III is 179 amino acids shorter than human protein, it lacks a large part of the lower domain. The loop between the two conserved zinc binding motives in the upper domain is 36 amino acids shorter and does not contain the ETGE motif, that is supposedly responsible for the binding of human DPP III to Keap1, a repressor protein from the Keap1-Nrf2 signalling pathway.

Cocrystal structures so similar even Rietveld is confused

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Ivabradine hydrochloride (IVA HCl) is an active pharmaceutical ingredient (API) indicated for the symptomatic treatment of chronic stable angina pectoris and chronic heart failure. Ivabradine hydrochloride exhibits extensive polymorphism: there are more than twenty polymorphs of IVA HCl described in patent literature. Also, other salts of ivabradine (oxalate, adipate, citrate etc.) are under patent protection.

We concluded that IVA HCl could also be prone to accommodate a coformer, thus providing a cocrystal. We performed a cocrystal screening and identified two cocrystals: ivabradine hydrochloride (S)-mandelic acid 1:1 (IClSM) and ivabradine hydrochloride (R)-mandelic acid 1:1 (IClRM). The cocrystal structures were successfully determined from single crystal X-ray diffraction data and the materials were characterized by other solid state analytical techniques, such as X-ray powder diffraction (XRPD), solid state NMR spectroscopy and DSC.

As a part of the characterization, we wondered, which cocrystal structure was preferred. To decide, we let IVA HCl mature in the slurries with excess of racemic mandelic acid. The resulting solids were measured by XRPD both on flat Si holder and in capillary (Bragg-Brentano and Debye-Scherrer configurations) and the phase quantification of the powder patterns was done by Rietveld refinement in Jana2006 and HighScore Plus software. However, the similarity of the two structures of IClSM and IClRM (similar unit cell parameters and overall crystal packing) resulted in the algorithm getting confused during the refinement. The limits of the Rietveld fit in this particular example will be discussed.
Synthesis, characterization and crystal structures of 2-benzothiazolylhydrazones.

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2-benzothiazolylhydrazones represent an important class of heterocyclic compounds with diverse pharmacological activities such as: antitumor, antimicrobial, antidiabetic, anticonvulsant and anti-inflammatory. 1, 2 Reactions of 2-hydrazinobenzothiazole and arenecarbaldehydes afforded four 2-benzothiazolylhydrazone derivatives of general formulas: Bzt–NH–N=C6H4–X and Bzt–NH–N=C10H6–Y (Bzt=benzothiazolyl, X = 2–OH (1), Y = 2–OCH3 (2), 4–OCH3 (3), 6–OCH3 (4)).

Prepared compounds are characterized on the basis of elemental analysis, IR spectroscopy, TGA measurements, powder diffraction method, single crystal X-ray diffraction method and 1H NMR spectral studies. Both amino 2–4 and imino 1 tautomeric forms of prepared 2-benzothiazolylhydrazones are found, leading to different supramolecular architecture of their crystal structures and are accountable for different biological activity. 3 The amino form of compound 2 enables assembling of molecules into 2D infinite chains of R2̇(8) and R2̇(6) hydrogen bonded rings via N–H···N and C–H···O intermolecular hydrogen bonds, respectively (Fig.1a.). The chains are cross over connected via π···π stacking interactions between phenyl and thiazolyl rings of neighbouring chains. The imino form of 1 shapes infinite helical C(4) chain via N–H···N hydrogen bonds between thiazolyl –NH group and the hydrazone nitrogen atom, supplemented by π···π interactions (Fig 1b.).

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Synchrotron powder diffraction methods

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Powder diffraction with synchrotron radiation has ample opportunities for the study of the structural features of various materials. One of the modern tasks in is to investigate microstructural changes occurring in low-temperature superconductors under irradiation by high-energy particles. Nb-based materials (Nb3Sn, NbTi) are now widely used to fabricate magnetic coils for generating strong and superstrong magnetic fields in various large experimental facilities, for example the modernization project of Large Hadron Collider (CERN, Switzerland) involves the use of Nb3Sn as a superconducting material of magnetic systems, which makes it necessary to examine the changes in its properties after irradiation by beams of fast particles (protons).

As it is known from the literature [1] the superconducting property changes of Nb3Sn under the influence of radiation are primarily associated with changes in its structure and in particular with the appearance of antisite radiation defects, when a part of Nb atoms goes to the Sn atomic positions and vice versa. The present work is dedicated to the study of appearing of antisite defects in the Nb3Sn samples under irradiation by fast protons.

Samples for the study were provided by a group of René Flückiger (CERN, Switzerland). Irradiation by fast protons with an energy of 12.8 MeV at room temperature was carried out at the cyclotron U-150 NRC “Kurchatov institute”. Measurements using X-ray diffraction in normal and resonant modes were carried out at the "Structural Materials science" beamline at Kurchatov synchrotron radiation source.

Photocatalytically active titania thin films and powders

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TiO₂ has been increasingly used as a photocatalyst in different environmental applications and solar cell manufacture 1. Heterogeneous photocatalytic oxidation is a promising technique for the complete oxidation of organic pollutants. The UV light excites electrons of the photocatalyst from the valence band into the conduction band, and the resulting electron/hole pairs can then migrate to the surface and initiate redox reaction with adsorbed organics 2. TiO₂ photocatalyst has been investigated in a powdered form (in a suspension), and supported as a thin film on various substrates. The latter form has become a better option as TiO₂ in slurry or suspension has to go through separation of dispersed particles after the treatment 3.

Thin films and corresponding xerogels were prepared by particulate sol-gel route from TiCl₄ precursor and stabilized by sulphuric or hydrochloric acid. Organic polymer hydroxypropyl cellulose was added to control the porosity of the prepared samples. A transparent sol is formed after hydrolysis of the precursor, which can be coated on the substrates and thermally treated at higher temperatures to promote crystallization of anatase phase.

A degree of thermal treatment is very important step in the preparation of efficient thin film or powders. Not only the crystalline phase (anatase, rutile, brookite), but also the size of the anatase grains determines the properties of the material. Two opposite effects were observed as particle diameter decreases: 1) specific surface area of the material increased and 2) in the semiconducting material recombination rate of photo-induced electron-hole pairs decreases due to faster arrival to the reaction site on the surface. On the other hand, there is an increase in the bandgap with decrease in the particle size meaning that shorter wavelength is needed for excitation.

X-ray diffraction is indispensable technique for determining the crystalline phase obtained after various thermal processing as well for determining the size of the nano-grains. For the latter, Scherrrer equation was used. Photocatalytic efficiency of thin films and powders, thermally treated to a different degree, was determined from the rate of methy-stearate degradation during UV-light irradiation.

Crystal Packing of Agomelatine in Its Various Solid Forms

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One of the main tasks of pharmaceutical solid state chemistry is the search for new solid forms, as they can offer advantageous physico-chemical properties important in the final drug formulation. Crystal structure solution offers invaluable information about many properties of the said materials. Our model compound is agomelatine, a melatonergic antidepressant. It can form many different phases. We have described several salts and co-crystals. As the number of crystal structures of this compound rises, it is becoming difficult to easily compare all of them and find their similarities and differences. We would like to present the comparison of molecular packing of agomelatine by two methods. One of the software used is being developed by our group. A new approach is introduced for comparison of molecular packing and for identifying identical crystal structure motifs. The similarity is calculated from a simple formula including intermolecular distances and relative orientations of molecules inside the finite molecular cluster. The other software is the Crystal Packing Similarity tool in the Materials module of Mercury. From both approaches, a similarity tree diagram is the final result. The tree diagram is used for a clear analysis of similarity in crystal packing of structures of one compound. It can compare the crystal packing of only the largest molecule in the structure (in our case agomelatine). Therefore, it can be easily used to analyze a family of polymorphs, hydrates, solvates, salts and co-crystals. Beside the difference in the calculation itself, the main difference between the two types of software is the convenience for the user. While the construction of a tree diagram based on data calculated in Mercury takes at least hours (first, several separate calculations are run, then the results can be processed by the user to a form of a diagram), our approach is much faster and more user-friendly, because the tree diagram is generated automatically.

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Versatile coordination behavior of 2,6-diacetylpyridine bis(S-methylisothiosemicarbazone) in transition metal complexes

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Thiosemicarbazones (tsc) are important class of S-donor ligands\(^1\). Their transition- and non-transition metal complexes have been studied for many years, mainly due to wide spectrum of their biological activity. Their S-alkylated derivatives—isothiosemicarbazones (itsc)—have been less studied, although they show interesting structural and electrochemical features. As a rule, isothiosemicarbazones are coordinated through the azomethine and isothioamide nitrogen atoms. However, 2,6-diacetylpyridine bis(S-methylisothiosemicarbazone) (H\(_2\)L) is one of the rare examples which shows several cases where this rule is not obeyed.

Several complexes with this ligand are known,\(^2-4\) five of which are structurally characterized: [Mn(H\(_2\)L)(NCS)MeOH]NCS (1), [Fe(HL)(N\(_3\))\(_2\)] (2), [Ni(HL)I] (3), [Cu(H\(_2\)L)Cl\(_2\)Py] (4) and [Cu\(_{10}\)(H\(_2\)L)\(_2\)Br\(_{10}\)Cu\(_6\)] (5). Here we present crystal structures of two copper complexes with this ligand of the formula [Cu(H\(_2\)L)(ClO\(_4\))\(_2\)]·Me\(_2\)CO (6) and [Cu(H\(_2\)L)(ClO\(_4\))\(_2\)] (7) where two novel coordination modes are observed.

Hitherto observed coordination modes of H\(_2\)L are summarized as follows (Fig.). Symmetrical pentadentate (N\(_5\)) coordination mode in neutral and monodeprotonated form is observed in 1 and 2, while tridentate (N\(_3\)) coordination mode is found in 4. In complexes 3 and 7 very unusual coordination of one isothiosemicarbazide moiety through the hydrazine nitrogen atom only is found, which leads to formation of six-membered metallocycle and unsymmetrical tetradentate (N\(_4\)) coordination. In complex 6 an unsymmetrical tetradentate (N\(_4\)) coordination mode in a different way is achieved, while in the complex 5 the unique pentadentate coordination (N\(_4\)S) occurs, with additional involvement of alkylated sulfur atom. It appears that coordination of terminal isothioamide groups can be avoided by introducing co-ligands with good donor capabilities; that coordination of alkylated sulfur atom is possible when acceptors are soft Pearson acids.

![Coordination modes](image)

Fig. Summary of 2,6-diacetylpyridine bis(S-methylisothiosemicarbazone) coordination modes

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Cocrystal screening of trospium chloride based on shape and polar surface of participating components

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Trospium chloride (TCI) is a drug used to treat urge incontinence and frequent urination. Structures of five co-crystals of TCI with various co-formers (glutaric acid, salicylic acid, oxalic acid, adipic acid and urea) were published. Twenty one coformers were selected for the cocrystal screening. Selection of these coformers was based on shape and polar surface similarity between the coformers and TCI. As the cocrystallization screening technique, slow evaporation of solution from three different solvents was used. In this work, single-crystal (SXRD) and powder X-ray diffraction (PXRD) were used for structure characterization and phase analysis. The solids obtained from the screening were analyzed by PXRD and 24 unique powder patterns were observed, representing new solid phases. Five of these new phases were successfully solved from SXRD or PXRD. Two of the determined structures were cocrystals: TCI cocrystal with benzoic acid and a co-crystal with aminobenzoic acid. The other three determined structures were a novel polymorphs or solvates of the coformers: diazastilbene monohydrate, cholic acid ethanol solvate and the new polymorph of methyl-4-hydroxybenzoate.

Fig. 1: asymmetric unit cell of cocrystal trospium chloride and benzoic acid

Ruthenium complexes with phosphine ligands

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Chemotherapy is one of the most widely used therapies for the treatment of cancer, with cisplatin as one of the most commonly used drugs. However, its severe side effects have encouraged research of metal-based drugs with improved properties. In recent years, ruthenium-based complexes have emerged as promising agents with anti-tumor and anti-metastatic properties. One of the newest classes of organoruthenium agents are based on the phosphine ligand pta, which was originally introduced to increase solubility. The original compounds containing this ligand, prepared by Dyson et al., have been shown to have good anti-metastatic properties.

In our previous research we have reported the synthesis, physico-chemical characterization and biological evaluation of organoruthenium complexes with diketonate ligands and the monodentate phosphine ligand pta. One of the main discoveries was the change in the mode of action based on the introduction of pta, which is probably owed by the resistance to hydrolysis that pta brings. Building on this research, more complexes bearing pta ligand have been synthesized and their structures determined by single crystal diffraction. Said complexes will further be biologically evaluated in a bid to elucidate the mode of action and the structure-activity relationship of the complexes.

3-pyrroline hydrates: in situ crystallization and structural investigations

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3-pyrroline (2,5-dihydropyrrole, C4H7N) is a cyclic amine, liquid at ambient conditions. Using the in situ crystallization technique\(^1\) assisted by IR laser focused radiation we obtained two hydrates of 3-pyrroline (three- and hexahydrate) presented in the figure bellow. The trihydrate crystallizes in P\(_{21}/c\) space group (V=690 Å\(^3\)) with H\(_2\)O molecules forming layers. The amine molecules are attached to these layers via N···O hydrogen bonds. The hexahydrate belonging to P\(_{21}/m\) space group (V=538 Å\(^3\)) contains 3D network of interacting water molecules. In the structure the amine molecules are incorporated to this network thus the hexahydrate is example of semiclathrate\(^2\). This structure is isostructural with hexahydrate of pyrrolidine\(^3\) - saturated analogue of 3-pyrroline. Contrary to the pyrrolidine hexahydrate however, corresponding structure with 3-pyrroline, does not undergo order-disorder phase transition. In all presented structures containing 3-pyrroline water molecules are disordered what manifests in alternative positions of hydrogen atoms similarly like in the hexagonal ice Ih crystal structure.

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References
Crystallographic study of cyclohexanohemicucurbit[n]urils and their complexes

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Cucurbit[n]urils (CB[n]) are a versatile family of macrocyclic molecules, which consist of reoccurring monomers, giving the core CB[n] a range of inherent symmetry elements. Our group has focussed on cyclohexanohemicucurbit[n]urils (cycHC[n]), by synthesising and characterising chiral (all-R,R) or (all-S,S)-cycHC[6] and (all-R,R)-cycHC[8].1,2 In a dynamic system, where multiple products are obtained, single crystal X-ray diffraction can be a valuable tool for structure elucidation. A new macrocycle i-(all-R,S)-cycHC[6] with one inverted monomer was obtained, which introduces an interesting crystallographic problem (Figure 1). The overall shape of the macrocycle deviates so little as a result of this modification, that the obtained chloroform solvate of i-(all-R,S)-cycHC[6] is isostructural to the solvate of the previously known (all-R,S)-cycHC[6].3 The inversion centre in the centre of the cycle renders the inverted monomer in i-(all-R,S)-cycHC[6] disordered between two symmetry-related positions, so that structure elucidation becomes inconclusive between a single-inverted product and a 1:1 mixture of doubly inverted and unmodified (all-R,S)-cycHC[6]. A similar case was recently confronted by Ayhan et al.,4 where the disorder in the crystal structure of hydroxylated CB[n] prevents an unequivocal assignment of the structures as mono-, dihydroxylated or unmodified cucurbiturils. Isostructural set of crystal structures was also obtained in our efforts to gain insight into the binding of anionic guests by (all-R,R)-cycHC[8]. The anion bound within the cavity of the cycHC[8] does not significantly change the shape of the host and the packing is thus directed mainly by the counter cations. Interestingly, using structurally similar tetrabutylammonium (TBA) and –phosphonium (TBP) salts gave crystals in the orthorhombic space group P212121 or monoclinic space group P21; respectively. The latter were in all cases found to imitate the higher Laue symmetry as a result of twinning by pseudomeroberdy.

Figure 1: The possible interpretations of the disordered X-ray structure of i-(all-R,S)-cycHC[6]

Transferability of selected supramolecular synthons from organic to metal-organic systems

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Directed supramolecular interactions (such as hydrogen and halogen bonds) have proven to be invaluable tools in the field of crystal engineering. In simple systems it is possible to predict the formation of supramolecular synthons when using these types of interactions. Problems concerning synthon prediction arise in more complicated systems where multiple competing donor and acceptor sites are present. If we want to harness specific interactions in such systems, without relying on chance, a means of predicting the interaction motifs needs to be developed.

One approach is using the relative strengths of donors and acceptors to predict the interactions between them and a general rule was proposed that the best donors will interact with the best acceptors.\(^1\) This method of prediction has shown merit but measuring the “strength” of donors and acceptors still remained a problem. Electrostatic potential maps mapped on total density surfaces obtained via quantum-mechanical calculations offered an elegant solution for donor/acceptor strength assessment. It was shown that in purely organic systems the molecules tend to interact so that the best hydrogen bond donor (ESP maxima) pairs up with the best acceptor (ESP minima).\(^2\)

Here we opted to test transferability of selected supramolecular synthons form organic systems to metal-organic environment, where additional competing acceptor sites are necessarily present. We focus our attention to those synthons that have already proven to be robust and reliable in purely organic systems. For this purpose we prepared a series of β-diketonato complexes of Co\(^{2+}\), Ni\(^{2+}\) and Cu\(^{2+}\) with simple and rigid heterocyclic ligands bearing functionalities capable of forming self-complementary and directional interactions with HB donors and acceptors being directly attached to the heterocyclic systems. Complexes were synthesized by solution methods and solvent assisted grinding. Single crystals were obtained either by slow evaporation from mother liquor or by liquid diffusion methods. Crystal structures were determined by single crystal X-ray diffraction experiments and DFT calculations were performed to assess the capacity of acceptors and donors present in them.

Our results have shown that selected synthons were transferable to the metal-organic system of our choice despite of the presence of additional competing acceptor sites, and following the best-donor/best-acceptor concept from organic systems.

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The oxime moiety in metal-organic systems: The cadmium(II) study case

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The way in which molecules interact to form highly-ordered 3D structures is one of the most interesting questions in materials science today. Understanding the relatively weak and reversible interactions between molecules can give us a great opportunity to target a desired physical property. The time and effort invested in research of intermolecular interactions in organic systems exceeds that spent on studying their metal-organic counterparts. The question is whether the supramolecular synthons, already proven as robust and reliable in the design of organic systems, can play the same/similar role in the supramolecular metal-containing architectures?

Our research is mainly focused on the idea of transferability of same or alike supramolecular motifs from organic to metal-organic systems. Here we have found the oxime moiety a promising supramolecular connector for that purpose due to its easily achieved tunability.1 To be used as a connector for metal-organic building blocks, we firstly equipped the oxime moiety with the pyridyl backbone to provide it with coordinating power thus leaving the oxime functionality unaffected and ready to form the same type of interactions as in pure organic systems. Furthermore, we opted for CdX₂ systems as these are known to form 1-D polymeric structures and consequently reduce the dimensionality of supramolecular interactions that needs to be controlled.

Hirshfeld surface analysis and detailed computational study, in addition to our structure determination results complemented by data mining, allowed us to get additional insight into intermolecular interactions responsible for the assembly of 1-D building blocks and transferability of the oxime motifs to these systems. Furthermore, by comparison of molecular electrostatic potential (MEP) maps and the calculated interaction energies between pairs of molecules we were able to identify the most prominent interactions. A set of tentative guidelines about the design of alike structures emerged and their validity should be addressed in future studies on other metal-containing systems.

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**Structural and stability studies of sodium formate monoperhydrate**

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The crystal structure of a novel solid state hydrogen peroxide carrier, sodium formate monoperhydrate, has been determined and compared to other sodium oxysalt perhydrates. Its decomposition under ambient conditions has been studied using PXRD, showing deperhydration to be the main mode of decomposition. At higher temperatures, TGA/DSC measurements showed that the title compound was completely transformed to anhydrous sodium carbonate in an exothermic oxidation reaction at 100° C.
The investigation of bonding and non-bonding interactions in flatland metal complexes

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It is interesting to observe that a number of the molecules that are crucial for life in our 3D world are themselves planar e.g. the DNA bases and heme. The focus of my research will be to study the structures of planar compounds containing π-systems.

2,4,6-Tris(2-pyridyl)-1,3,5-triazine (tptz) is a bulky heterocyclic organic compound composed of three 2-pyridyl rings and a 1,3,5-triazine ring with an extended conjugated π system, Figure 1. It has been shown that tptz is a planar molecule with large stabilizing π systems. As a result of the aforementioned features of tptz, it draws much of the attention among the polypyridyl ligands. The tptz ligand is believed to be stable towards nucleophilic attack and has been found to form metal complexes in which the tptz acts approximately as a planar tridentate ligand. It has, therefore, been used as an analytical reagent for various metal ions. The tptz metal complexes continue to be the subject of extensive research due to their biological activity and their physical, magnetic and photoluminescence properties.

The project presents the synthesize and structural characterisation of three illustrated novel tptz metal complexes, [Cu(tptz)Cl\(_{2}\)(CH\(_3\)OH)]\(_{1}\), [Ni(tptz)Cl\(_{2}\)(CH\(_3\)OH)]\(_{2}\) and [Cr(tptz)Cl\(_{3}\)(CH\(_3\)OH)]\(_{3}\). Solid-state structures of the above complexes have been determined by single-crystal X-ray diffraction as a primary technique. The research has been started by looking through Cambridge Crystallographic Database (CSD) for similar structures to be compared. The research will look at the stereochemistry around the metal centre; also it will be interesting to observe the type of non-bonded interactions that can occur with extended planar aromatic systems.

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![Diagram of tptz ligand and complexes](image.png)

the tptz ligand  complex 1  complex 2  complex 3
X-ray microstructural characterization of gelatin/hydroxyapatite scaffolds for osteochondral defect repair

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An osteochondral defect is a damage affecting the articular cartilage and the underlying (subchondral) bone. Several efforts have been made aiming at overcoming traditional clinical methods for the treatment of bone and cartilage injuries. Promising results have been obtained with the tissue engineering approach by developing scaffolds that mimic the osteochondral tissue. Here a 3D osteochondral scaffold made of a gradient of hydroxyapatite (HA) at 30wt% embedded into a bovine gelatin matrix, fabricated by an in situ sol-gel synthesis¹ is characterized by two different techniques exploiting X-ray radiation, with table-top setups: micro-tomography (micro-CT) and microdiffraction.²³ MicroCT characterizes the material microstructure in the three dimensions at the micron scale spatial resolution, whereas microdiffraction allows to have a combined structural/morphological information on the atomic and nanoscale structure, with hundred microns spatial resolution. The combination of these two techniques allows a complete structural characterization of the scaffold, determining the HA crystalline phase into the gelatin and confirming the presence of a HA gradient across the longitudinal axis of the scaffold.

Quantum-chemical calculations have been successfully used to complement the experimental X-ray powder diffraction (XRPD) data at several stages of the structure solution process: (1) To optimize the molecular geometry in the gas phase to obtain accurate starting molecular structure suitable for structure solution by real space methods. In this stage different levels of theory are applied: molecular mechanics, semi-empirical methods, Hartree-Fock methods, density functional theory (DFT). (2) To minimize the energy of crystal structure and provide reasonable bond lengths and angles to input into the Rietveld refinement as chemical restraints. Calculations are performed using plane wave DFT with dispersion correction (DFT-D). (3) Because it is difficult to accurately locate the positions of H atoms from the XRPD data, energy optimization provides the most reasonable approach to compute optimal positions for the H atoms as the final step, with unit cell and non-H atomic positions fixed to those established by Rietveld refinement1. (4) To clarify an ambiguity concerning the orientation of functional group that could not be distinguished on the basis of the XRPD data alone2. (5) Geometry optimization with DFT-D approach in the solid state has been applied to refine the crystal structure when Rietveld refinement yielded inaccurate molecular geometry, providing results whose accuracy is comparable to that of single-crystal refinement3. (6) To assess the correctness of experimental organic crystal structures4. EXPO20145 provides crystallographers with tools to make theoretical molecular calculations feasible: (a) Preparing input files and reading molecular geometry from output files of a wide variety of computational chemistry packages (GAMESS, NWChem, Gaussian, and others)6–8. (b) Optimizing the geometry of molecule by molecular mechanics using Open Babel’s force fields9. (c) Providing graphical interface to run semi-empirical quantum calculation by MOPAC10. (d) Input file for DFT-D can also be produced.

High capacity Li-rich cathode materials

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The need for better batteries has never been greater. In the application of electrical vehicle, automotive manufacturers require lithium batteries with more advanced performance than it is now. Lithium batteries may also play a critical role in de-carbonization of the electricity grid. Lithium rich layered cathodes, which offer increased capacity and higher operation voltage, have, for several years, been regarded as the next major advance, but they are still challenged by problems such irreversible first cycle capacity, voltage fade on cycling related to changes in the structure. Recently important work has been carried out to better understand the origin of the high capacity and the voltage fade.

In this contribution we shall present a new sol-gel synthesis for compositions such as $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ and discuss their limitations and operation. The cycling stability of the material is extremely good with a capacity of $\sim 250 \text{mAh g}^{-1}$ maintained after 100 cycles.

Figure 1. Load curve and cyclability data of sol-gel prepared $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ at a rate of 50 mA h g$^{-1}$
Using the Cambridge Structural Database (CSD) for Education

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The Cambridge Structural Database (CSD) contains over 800,000 small molecule crystal structures, curated and maintained by the Cambridge Crystallographic Data Centre (CCDC). The CSD is the go-to resource for structural chemists worldwide and can also serve as a resource for educators teaching both crystallography and chemistry. The CSD provides three dimensional structures and a wealth of statistical information about symmetry, packing, coordination environments, bond distributions, and intermolecular interactions. We can illustrate a huge variety of chemical and crystallographic principles using the information in the CSD.

This poster will focus on the ways educators can use crystal structure data and CSD tools in the classroom to augment the learning experiences of students in schools and universities worldwide.
Development of room temperature serial crystallography at ESRF, ID13

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Structure determination of membrane proteins remains one of the critical steps to be mastered before achieving breakthroughs in life science and medicine. This is mainly due to intrinsic problems with growing stable crystals, which are suitable for structure analysis using standard X-ray crystallography techniques. But recent developments of serial crystallography at the synchrotrons, such as new sample mounting systems1,2, ultra-fast detectors (EIGER), an intense, small X-ray beam and computational infrastructure to process the large volume of data, are making it possible to collect a large number of short exposures in situ from microcrystals at room-temperature.

One of the methods to develop serial crystallography of membrane proteins is lipidic cubic phase (LCP) microjet-based serial millisecond crystallography at third generation synchrotrons, similar to serial femtosecond crystallography (SFX) at X-ray free electron lasers (XFELs). The main advantages of the method are: crystal injection using LCP-jets combined with a microfocus beamline allows diffraction data to be collected at room temperature, without crystal freezing and difficult crystal handling steps (such as mounting crystals in a loop); thousands of crystals can be screened in a short time and with less than a milligram of protein; microfocus beams at storage ring sources are widely available and finally the method is well suited for time-resolved diffraction studies on the microsecond to millisecond time scale. The LCP-jet method has been recently demonstrated by solving a structure of the light-driven proton-pump bacterio-rhodopsin at a resolution of 2.4 Å.

Another innovation is to perform serial crystallography at room-temperature using CrystalDirect plates that were created at HTX-lab in EMBL, Grenoble3. These plates allow to grow crystals on very thin films that can then be excised with a laser beam to recover the crystalline material. Due to their design, CrystalDirect plates allow to collect diffraction data in-situ with very low background. CrystalDirect systems offer a lot of advantages, like absence of the mechanical stress for the crystals (no tools enter the crystallization drop), full automation of the crystal-harvesting process, availability to know in advance all positions of the crystals, systematic testing the large numbers of crystals.

Alternative approach is based on scanning micro-crystals, which are deposited on solid supports 1. First successful results have already been obtained using micro-crystals. Future possibilities for optimization, including humidity controlled gas sample environments, and the potential of room temperature scanning serial crystallography for observing macro-molecular dynamics will be discussed.

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Polarization of the transferred electron density of a protein-ligand complex toward improving enthalpy calculations based on multipolar electrostatics.

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The scope of this work is to assess the transfer of multipolar electron density on protein structures to extrapolate some of their properties, here the rigid-body interaction energy between members of a protein-ligand co-crystal in the absence of solvent. The transferable multipolar parameters originate from highly accurate charge density studies of organic small molecules structures. These parameters don't take into account the inhomogeneous electric fields found in proteins. However it is believed that atomic polarization contribute significantly to the electrostatic interaction in such protein ligand complexes. Hence, to account these local influences at the dipole level, we used the J.Applequist1 and B.T.Thole2 formalism allowing the determination of induced dipoles on each atom in response to an external electric field. Those induced dipoles are then included3 in the electrostatic contribution of the protein-ligand interaction energy. Since this method uses a \(3n^2\) matrix inversion for \(n\) atoms included in the polarization process, the use of Coupled Polarization matrix Inversion and Iteration (CPII)4 is needed to obtain polarization of the whole protein in a reasonable time. CPII is based on splitting the protein in smaller regions, allowing fast matrices inversions, before re-evaluation of the external electric field induced on each region. This process is iterated until induced dipole moments reach numerical stability (under a given threshold). Atomic polarizabilities and screening factors are parameters inherent to the interacting dipole formalism1,2. To fit them, along with compatible van der Waals parameters, we use a custom database, where Isothermal Titration Calorimetry (ITC) experiments results found in the literature are paired with the most relevant Protein Data Bank structures (n=58 couples). The choice of ITC is motivated by the access to experimental binding enthalpies, which are expected to be more closely related to the calculated contribution (sum of electrostatics and van der Waals) than inhibition or dissociation constants. Polarizabilities and atomic van der Waals parameters for non-organic atoms were taken from the literature. To avoid statistical bias, the database is stratified on crystallographic precision (evaluated by their Diffraction Precision Index5), ligand structure categories and sequence homology.

Purine nucleoside phosphorylase from bacterium Helicobacter pylori: Cloning, Expression, Purification and Crystallisation

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Purine nucleoside phosphorylase (PNP) is the key enzyme in the purine salvage pathway. It catalyses the reversible phosphorolytic cleavage of the glycosidic bond of ribo- and deoxyribonucleosides, in the presence of inorganic orthophosphate as a second substrate to generate the purine base and ribose(deoxyribose)-1-phosphate. There are PNPs with differing specificities which can be divided in two main classes, low-molecular-mass homotrimers specific for catalysis of 6-oxopurines and mostly found in eukaryotes and some bacteria, and high-molecular-mass homohexamers with broader specificity for both 6-oxo-and/or 6-aminopurines and are characteristic for bacteria.

*Helicobacter pylori* is a Gram-negative, microaerophilic bacterium, human pathogen involved in development of many diseases as gastric ulcers and stomach cancer, and therefore known for its ability to colonize human stomach. Study of the *H. pylori*, due to the evergrowing infection rate and increase of *H. pylori* antibiotic resistance, is centered on understanding pathogenesis and finding a way to attack and eradicate *H. pylori*.³

Purine production is required for DNA and RNA synthesis and directly affects growth for both prokaryotic and eukaryotic cells – *H. pylori* cannot synthesize purine rings through de novo pathway and has to rely on purine production through purine salvage pathway.¹

Purine nucleoside phosphorylase gene *deoD* was isolated from genomic DNA of *Helicobacter pylori* (strain 26695) and amplified using Phusion High-Fidelity PCR kit with the set of specific DNA primers for both 5’ and 3’ ends of the gene. Resulting plasmid pet21b-HP26695deoD, with ampicillin resistance and without purification tag, was transformed into *E.coli* strain RIL+. Induction conditions for PNP expression in E.coli were optimised and evaluated by SDS-PAGE electrophoresys of bacterial cultrate filtrate.⁴

Purification of overexpressed PNP from the bacterial culture filtrate was preformed by anion exchange chromatography on Q-Sepharose FF column. Next step, which gave single protein band on SDS-PAGE was affinity chromatography, performed on Sepharose-formycinA column. Biochemical characterization involves, and is ongoing, kinetic studies, temperature and pH effects on stability and activity of PNP. Crystallisation experiments with purified purine nucleoside phosphorylase from *H.pylori* are underway.

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MgAl$_2$O$_4$ nanoparticles from thermal decomposition of metal-triethanolamine complexes: the effect of calcination temperatures and samarium content on luminescence characteristic

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Magnesium aluminate spinel phosphors doped with Sm$^{3+}$ (MgAl$_2$O$_4$: Sm$^{3+}$) were prepared by thermal decomposition of metal-triethanolamine complexes. The complexes were synthesized by simply mixing triethanolamine with nitrate salts in ethanolic solution. Then, the obtained complexes were subjected to calcining at various temperature (800, 900, 1000, 1100 and 1200 oC) for 2 h. The calcined powders were characterized by FT-IR, XRD, FE-SEM, TEM, XAS and PL. XRD patterns revealed that the main crystalline phase of the calcined powders was MgAl$_2$O$_4$ spinel and no impurity phase of Sm$_2$O$_3$ was observed. This suggested that the samarium ions might be substituted in the lattice points of the MgAl$_2$O$_4$ host. FT-IR spectra showed two peaks of the vibration according to the lattice of MgAl$_2$O$_4$, consistent with the XRD data. Moreover, the XRD peaks were also used to calculate the crystallite sizes by Scherrer’s equation. It was found that the crystallite size got larger as the calcination temperature was increased which was related to the larger in particle sizes observed from FE-SEM and TEM. XANES study illustrated that the samarium ions doped in the magnesium aluminate spinel were Sm$^{3+}$ due to the same edge energy as the standard Sm$_2$O$_3$. From the photoluminescent study, all the prepared phosphors exhibited the emission peaks at 598 nm ($^4$G$_{5/2}$ → $^6$H$_{7/2}$) and 644 nm ($^4$G$_{5/2}$ → $^6$H$_{9/2}$), under excitation at 280 nm. These transitions were due to the electronic relaxation of the Sm$^{3+}$ system so that the results were in line with XANES study. Besides, the luminescence intensity of the peak were decreased as the calcination temperature increased. This observation can be explained by in terms of the local structure of samarium ions studied by EXAFS. The greater the crystallinity of the Sm$^{3+}$ local structure, the lower the luminescent intensity. Therefore, in this study, the maximum luminescence intensity was observed for the phosphors calcined at the temperature of 800 oC. Furthermore, the optimum Sm$^{3+}$ concentration was 1 mol% as the luminescent intensity did not increase significantly for Sm$^{3+}$ content higher than 1 mol%.

Spectroscopic, thermogravimetric and x-ray study of copper and cobalt complexes with 2-pyrazinecarboxylic acid

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In the frame of our previous works we studied the effect of over 40 metal cations on the electronic system, physicochemical and biological properties of different ligands – derivatives of benzoic acids¹–⁴. The complexations of aromatic carboxylic acids by metal cations changes the electronic charge distribution within the aromatic ring and the carboxylate anion. So far, our studies showed that the effect of metal cation on the electronic structure of pyridine ring of pyridinecarboxylic acids depends on the position of nitrogen atom within the carboxylic acid structure. In the frame of this work the complexes of 2-pyrazinecarboxylic acid with cobalt and cooper were synthesized as well as the x-ray diffraction, spectroscopic (FT-IR) and thermogravimetric studies of obtained compounds were done. The FT-IR spectra were recorded with an Alfa (Bruker) spectrometer within the range of 400–4000 cm⁻¹. Samples in the solid state were measured in KBr matrix pellets and ATR technique. The products of dehydration and decomposition processes were determined from the TG curves.


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Thermogravimetric research was performed at the Center of Synthesis and Analysis BioNanoTechno of the University of Białystok. The equipment in the Center of Synthesis and Analysis BioNanoTechno of University of Białystok was funded by the EU, project: POPW.01.03.00–20–034/09–00.
Spectroscopic, X-ray and thermogravimetric study of zinc2-pyrazinecarboxylate

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In the frame of this work the complex of 2-pyrazinecarboxylic acid with zinc was synthesized. The zinc 2-pyrazinecarboxylate was prepared in water solution by adding sodium salt of ligand to appropriate amount of zinc chlorides at 80°C, continuous stirring for two hours (molar ratio of sodium salt of ligands to the zinc chloride was 2:1. The mixtures were left for 24 hours at room temperature. After one day received white crystals. X-ray diffraction, spectroscopic (FT-IR) and thermogravimetric studies of obtained compound were done. X-Ray diffraction data were collected at 100 K and crystal structure was solved and refined. The FT-IR spectra were recorded with an Alfa (Bruker) spectrometer within the range of 400–4000 cm⁻¹. Samples in the solid state were measured in KBr matrix pellets and ATR technique. The products of dehydration and decomposition processes were determined from the TG curves. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo Star TGA/DSC1 unit. Argon was used as a purge gas (20 mL•min⁻¹). Sample were placed in aluminum pans and heated from 50°C to 850°C with a heating rate of 10°C/min.

![Fig.1. The structure of hydrated complex of zinc 2-pyrazinecarboxylate.](image)

Studies have been carried out in the framework of the work no. S/WBiIŚ/1/2012 and financed from the funds for science MNiSW. Thermogravimetric research was performed at the Center of Synthesis and Analysis BioNanoTechno of the University of Białystok. The equipment in the Center of Synthesis and Analysis BioNanoTechno of University of Białystok was funded by the EU, project: POPW.01.03.00–20–034/09–00.
The crystal structure of calcium complex of 2,5-dihydroxybenzoic acid (gentisic acid): synthesis, XRD, XRDP, spectroscopic (IR, Raman, NMR) and biological studies

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2,5-Dihydroxybenzoic acid (gentisic acid) belongs to the group of plant antioxidants that are extensively studied due to their possible application in medicine, pharmacy or food industry. Because free radicals are constantly formed in our body during normal metabolism as well as pathological states it is necessary to maintain the proper balance of free radicals production and antioxidant defense system. The oxidative stress is considered a major cause of inflammatory, ischemic and neurological diseases, atherosclerosis, different types of cancer and aging process. Hence the natural nontoxic antioxidants (or their derivatives) may play an important role in the therapy of these diseases.

The structure and composition of the resulting complex (Fig. 1) were studied by single-crystal and powder X-ray diffraction. Single-crystal X-ray data revealed that the compound crystallizes in the orthorhombic space group Pbcn. The Ca(II) cation is coordinated in a monodentate fashion by two symmetry-related gentisate anions and five water molecules. The metal ion and one of the water molecules are located on a 2-fold rotation axis. The adjacent monomeric units are assembled into a 3-D supramolecular framework via O-H...O hydrogen bonds. Comparison of the experimental X-ray diffraction powder pattern with that simulated from single-crystal X-ray data confirmed the purity and homogeneity of the sample. The FT-IR, FT-Raman, UV/VIS, ¹H and ¹³C NMR spectra of calcium 2,5-dihydroxybenzoic acid were registered and analyzed. Moreover the effect of calcium complex and 2,5-dihydroxybenzoic acid on basic oxidative stress parameters, such as thiol group content and lipid peroxidation was studied. The antiradical and ferric reducing power of these compounds was measured by DPPH, ABTS and FRAP method.

Figure 1. Molecular structure of the calcium complex of 2,5-dihydroxybenzoic acid.

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Spectroscopic and crystallographic study of selected phenolic compounds

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In our previous papers we investigated the influence of metals on the electronic structure of biologically important ligands, such as aminobenzoic and picolinic acids as well as chosen phenolic acids. Presently we study correlations between the molecular structure and electronic charge distribution of compounds and biological activity of these compounds and their metal complexes. This research is aimed on finding new, more effective and selective substances exhibiting cytostatic or antioxidative properties. The proposed approach is also intended to reveal, if metal complexation can improve the activity and selectivity of some anticancer ligands.

The aim of the present work, being a part of the above mentioned wider context research is: (1) to collect complementary data describing the molecular structure and electronic charge distribution (determining biological properties) of some chosen phenolic compounds, (2) analysis of correlations between the spectroscopic, X-ray diffraction data and quantum chemical calculations describing the molecular structure of phenolic compounds.

In our work we applied the following research methods: vibrational spectroscopy (FT-IR, FT-Raman), mass spectrometry (MS), nuclear magnetic resonance (1H NMR, 13C NMR, as well 2D), electronic absorption spectroscopy (UV-Vis), spectrofluorometry, X-ray diffraction and quantum chemical calculations.

Studied were phenolic compounds and flavonoids comprising so called “logical series of ligands” – wherein each subsequent ligand differs from the previous one with a particular functional group. For example: flavone, 3-hydroxyflavone, 3,5-dihydroxyflavone, 3,5,7-trihydroxyflavone, 3,5,7,3’-tetrahydroxyflavone, quercetin.

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Interplay between structure, microstructure and magnetic properties of the CoMn$_2$O$_4$ spinel material

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Complex metal oxides, especially those crystallizing in the spinel-type family AB$_2$O$_4$, represent an important class of the functional materials, which as a result of their unique chemical, electric, magnetic and mechanical properties have wide range of potential applications ranging from energy storage and conversion to magnetism, electronics and catalysis. Among large number of different spinel materials, cobalt manganite (CoMn$_2$O$_4$) attracted great attention as new advanced anode material for lithium-ion batteries, electrocatalysts for oxygen reduction/evolution reactions and catalyst in CO oxidation. Majority of recent work appears to be strongly focused on electrochemical properties i.e. applications of the CoMn$_2$O$_4$ oxide as high capacity and high performance anodes LiB, while the structural and magnetic studies have been scarce in spite of few papers reporting on very intriguing and complex but still poorly understood magnetic behaviour.

CoMn$_2$O$_4$ samples were prepared by thermal decomposition of single-molecular precursor $\{[\text{Co(bpy)}]_3[\text{Mn}_2\text{(C}_2\text{O}_4)_3]\cdot\text{H}_2\text{O}\}_n$ at various temperature: 500, 700, 800 and 1000 °C. Rietveld structure refinement showed that the increase of decomposition temperature causes prolongation of the octahedral bond lengths $d(\text{M}_{\text{oct}}-\text{O})$ and shortening of the tetrahedral once, $d(\text{M}_{\text{tet}}-\text{O})$. Decrease of metal-oxygen interatomic distances resulted from thermally enhanced substitution of $^{\text{tet}}\text{Co}^{2+}$ by smaller $^{\text{tet}}\text{Mn}^{3+}$ cations at A site (4$a$) of spinel structure. On the other hand, octahedral B site (8$d$) becomes partially occupied by $^{\text{oct}}\text{Co}^{2+}$ as a consequence of transferred Mn cations from octahedral to tetrahedral site. Changes in temperature of heating, besides influencing the structural features within crystal lattice, also had a strong impact on microstructural properties of prepared samples. Size-strain analysis performed during Rietveld refinement showed that average crystallite size of CoMn$_2$O$_4$ can be easily tuned in range of 8–40 nm.

The temperature dependence of magnetization, $M(T)$, of all prepared oxides was measured in different magnetic fields, in the temperature range 2–330 K. Two modes of measurement were applied: after cooling in zero-field (ZFC), and after cooling in magnetic field (FC) in which measurement is performed during heating. The field dependences of magnetization, $M(H)$, i.e. magnetic hysteresis loops, were measured at several stable temperatures in fields up to 50 kOe. Our results show that it is possible to switch between the superparamagnetic and ferrimagnetic behaviour of CoMn$_2$O$_4$ and even to tailor the characteristic magnetic transition temperatures, i.e. the boundaries between the hard and soft magnetic behaviour. The work was financed by the Croatian Science Foundation grant no. IP-2014-09-4079

Tavorite-type materials at the positive electrode of Lithium-ion batteries.

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Polyanionic materials attract a strong interest in the field of Li-ion battery research thanks to the wide range of compositions, structures and electrochemical properties they offer. The higher electronegativity of the polyanionic groups versus that of oxygen tends to increase, by inductive effect, the difference of potential with lithium reference of a given redox couple versus that observed in oxides.\textsuperscript{1} Among the variety of bi- or three-dimensional frameworks available, Tavorite-type compositions A\textsubscript{n}M\textsubscript{X}O\textsubscript{Y} (A = Li, Na; M = V, Fe, Mn, Ti ...; X = P, S and Y = O, F, OH, H\textsubscript{2}O) offer a very rich crystal chemistry.\textsuperscript{2} This structure is characterized by octahedral chains of transition metal cations [Y-MO\textsubscript{4}-Y]\textsubscript{∞} bridged by corner-sharing XO\textsubscript{4} tetrahedra, in such a way to generate a three dimensional framework in which alkali cations can diffuse easily. Their operating potential is tailored as illustrated in figure 1, “playing with” the inductive effect of the bridging anion Y in addition to that of the XO\textsubscript{4} group.

![Tavorite structure and working potential](image)

Figure 1: Representation of Tavorite structure and working potential of Tavorite-type AMPO\textsubscript{4}Y compositions.\textsuperscript{2}

The stabilization of new Tavorite-type compositions is therefore a major issue both at practical and fundamental levels. A combination of diffractions (Synchrotron X-ray, Neutron, and electron diffractions) and spectroscopies (NMR, IR and XAS) was used to characterize the atomic layout and the microstructure, and to highlight the presence of local defects which greatly affect the electrochemical properties. Moreover, \textit{in-situ or operando} (during the battery operation) experiments, using high resolution powder Synchrotron X-ray diffraction and neutron diffraction, are essential to get an in-depth understanding of the structural modifications involved during the alkali insertion/extraction reactions into/from the host structure, and to fully determine the phase diagram. The formation of alkali and/or charge orderings, which can be highlighted by the appearance of superstructures or modulations, allows a better understanding of the transport properties. In this poster a series of several new Tavorite phases (LiVPO\textsubscript{4}OH,\textsuperscript{3} LiVO\textsubscript{4}F\textsubscript{1-x}O\textsubscript{x} and NaVPO\textsubscript{4}F) will be presented.

Coordination-modulation assisted stepwise liquid phase epitaxial growths of metal-organic framework thin-films on quartz crystal microbalance (QCM) substrates

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Metal-Organic Frameworks (MOFs), or porous coordination polymers (PCPs), have been extensively investigated during the past decade due to their outstanding porosity, chemical modularity and structural diversity.1 In addition to tuning of the composition of MOFs, their physical form in the mesoscopic and macroscopic scales is known to uniquely affect their properties. The structuring of MOFs in two-dimensional superstructures (e.g. thin films) is an emerging field that has received an increased attention over the last few years due to their potential use in membranes, coatings, quartz crystal microbalance (QCM)-based sensors and microcantilever-based sensors.2 Among diverse synthetic methods used for fabrication of MOF thin films, stepwise liquid phase epitaxial growth (LPE) is one of promising methods to fabricate precise-controlled MOF thin films even at relatively low temperature. We were successful to fabricate the moisture-tolerant [Zn4O(L)3]n (L= dialkyl-substituent carboxypyrazolate derivatives) MOFs on the self-assembled monolayer (SAM) modified gold-coated QCM substrates. However, the observed growth behaviour is diverged from a self-terminated growth, resulting in micrometre-thick MOF films with moderately controlled crystalline orientation.3 Herein, we propose an improvement of the synthetic procedure by applying coordination modulation (CM) technique4 into the typical LPE method, so-called coordination-modulation assisted stepwise liquid phase epitaxial growth (CM-LPE). The presence of acetic acid as a modulator plays a role in altering the coordination equilibrium between metal SBUs and organic linker, which therefore affects the kinetic LPE growth of MOF thin films. Generally, the presence of modulator in the reaction retards the high degree of nucleation at the early stage whereas enhances the growth of the preformed nuclei into well-defined particles. However, the higher mole ratio of modulator retards the kinetic deposition of the MOF thin film on the substrate, resulting in less amount of deposited MOF film on the substrate surface. It is noted that using an optimal mole ratio of modulator during the LPE fabrication improves the crystallinity of the obtained MOF thin films and controls the crystallographic orientation along the film growth direction. Moreover, the methanol total adsorption capacity of the CM-LPE fabricated MOF films is significantly enlarged because of a higher contribution of the effective mass (or the highly-crystalline MOF component) on the QCM substrate. This integrated CM-LPE method opens the way to fabricate high-quality MOF thin films on the given substrates in a precise-controlled manner.

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Crystal and molecular structures of crystal forms of memantinium hydrogenmaleate

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In continuation of our study1,2 on alternative pharmaceutically acceptable salts3 of memantinium chloride (drug used for the treatment of Alzheimer’s disease) two crystal forms of memantinium hydrogenmaleate were prepared: a monohydrate form and an anhydrous form. Molecular and crystal structures of both crystal forms were determined via single crystal X-ray diffraction.

While memantinium hydrogenmaleate crystallizes in a monoclinic space group P21/n, its monohydrate form crystallizes in an orthorhombic space group Aba2, having two times bigger unit cell volume with respect to the anhydrous form (V = 1668.83 Å³ vs V = 3339.4 Å³).

Both crystal structures are characterized by complex hydrogen bonded networks involving protonated amino groups of memantinium cations and hydrogenmaleate anions. In the anhydrous form, each amino group forms three somewhat comparable hydrogen bonds of the N–H···O type with the surrounding hydrogenmaleate anions. In the monohydrate form, protonated amino group realizes three hydrogen bonds of the N–H···O type, two of which involve hydrogenmaleate anions, while the third one embraces a water molecule. Moreover, the presence of water molecule, and its simultaneous role as a hydrogen bond donor and acceptor, results in a greater variety of hydrogen bonding motifs in the monohydrate form as compared to the anhydrous form (Figure 1).

![Figure 1. Crystal packing in memantinium hydrogenmaleate, monohydrate form, viewed down the a-axis.](image)

1 Tuksar, M., Žegarac, M., Brdar, B., Lekšić, E., Meštrović, E. 23th Meeting of Chemist and Chemical Engineers, Book of Abstracts, Osijek, 2013, p. 117.
Advances in imaging of small virus particles at an X-ray laser

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The very short and intense pulses of recently developed X-ray lasers provide the possibility to study the structure of non-crystalline single biomolecules and virus particles using coherent diffractive imaging techniques based on the principle of “diffraction before destruction”\(^1\). This technique has been successfully applied for 2D imaging of mimivirus particles\(^2\), cell organelles\(^3\) and living cells\(^5\). However, both for large macromolecules and small virus particles the measured signal intensity as of today is not sufficient to obtain structures from a single-shot experiment.

However, there is great potential for a successful reconstruction of the three-dimensional structure by combining many randomly oriented single-shot diffraction patterns from a sample of reproducible particles and computationally solve the orientation problem prior to phase retrieval\(^6\). For mimivirus, a virus 500 nm in diameter, this approach has been experimentally proven recently\(^5\). As we are approaching smaller particles, e.g. viruses in the 30-100 nm range, data reduction and pre-selection of diffraction patterns becomes more challenging. We therefore developed fast computational methods for robust and nearly automated feature extraction (size, intensity in the beam focus, scattered intensity) based on single-shot diffraction data of small biological particles with low signal. In this work, we present the current state of small viruses imaging using an X-ray laser. Data has been collected at the Coherent X-ray Imaging (CXI) beamline at the Linac Coherent Light Source (LCLS)\(^7\). Diffraction measurements of Omono river virus (\(~40\) nm) were taken at 5.5 keV photon energy.

Being able to provide reliable information about the size of injected particles (Figure 1) and other features prior to orientation recovery and reconstruction procedures as well as providing real-time feedback during data collection is an important step toward the aim of revealing the inner structure of small viruses with X-ray lasers.

Figure 1. Selection of 8 diffraction hits (out of 9 576) showing a variety of different diffraction patterns collected at CXI beamline of the LCLS. Masked values are shown in gray.

Metal-Hydride Organic Frameworks: synthesis and structure

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Clean and easy production from water and renewable energy classifies hydrogen as a great candidate for energy carrier. Problem of safe and efficient storage of hydrogen can be solved by solid state storage either through chemical bonding in crystalline compounds or by physical adsorption in porous materials. [1] A novel hybrid materials, metal-hydride organic frameworks (HOFs) are designed by interweaving of molecular building blocks of light-weight complex hydrides with organic linkers. Flexibility of the borohydride anion allows other cation coordination than usually available in coordination frameworks what results with great HOF’s properties (guest-host interactions, dehydrogenation properties). Also, advantage in this design is possibility to use direction al anionic ligands other than hydrides and for this purpose we used imidazoles and its derivatives because the metal-imidazolate-metal angle of 145° is very similar to metal-borohydride-metal angle observed in Mg(BH4)2. [2]

Standard ball-milling procedure under inert atmosphere was used for sample preparation. Two synthetic routes were explored, a solvent free and liquid-assisted grinding with different solvents (DMF, DMSO, THF, acetonitrile). [3] Chemicals used in synthesis were NaBH4, NaIm, MgBH4, HIm, 2-MeIm, ZnCl2 or other metal cations as starting reactants. First results on mono- and bi-metalic mixed anion (borohydride and imidazolate) frameworks based on Zn2+ and light alkali (Li+, Na+) or earth alkali (Mg) metal cations will be presented.

Final products are polycrystalline and usually containing several novel crystalline phases of uncertain chemical composition, so we performed synchrotron high temperature in-situ powder diffraction measurements on prepared compounds (T-ramping). [4] Structure solution was carried out by combining information obtained from electron density maps provided by Direct Methods and several direct space approaches such as Simulated annealing and Parallel tempering. [5] Results on change of microstructural parameters under the influence of temperature and results of NMR solid state measurements will also be presented.


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Racemates and Optical Activity

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Racemates have been assumed to be optically inactive for the last 160 years. The cancelation of opposite optical rotations from left- and right-handed enantiomers (racemates) was discussed by Pasteur for tartaric acids and has never been dismissed. However, Pasteur opened a question: "En est-il toujours ainsi? C'est à l'expérience de répondre" which could be translated as "Is it always true? The experiments should tell us". In this poster, we will show that specific arrangements of racemic units in the solid-state can lead to optical activity and that as many as one in twenty racemic compounds are potential optically active materials.1 Indeed, the enantiomers of opposite handedness can arrange into the 21 non-enantiomorphous point groups while optical activity can be described in the eleven enaniomorphous point-groups and four non-enantiomorphous point-groups (Figure 1(a)). Thus, the "optical activity" and "Racemic compound" groups are not independent. The optical activity from racemic materials has been confirmed by the measurement of single-crystal circular dichroism on two compounds crystallizing in the point-group mm2 (Figure 1(b) and (c)). In these crystal structures, the arrangement of these units is a key to breaking the centrosymmetry and leads to the presence of optical activity.

![Figure 1](image)

Figure 1. (a) The 32 crystallographic point groups and optical activity, Centrosymmetric = Black, Polar/Non chiral = Red, Chiral/Non polar = Blue, Chiral/Polar = Purple, Noncentrosymmetric/Non chiral/ Non polar = Green). Circular dichroism spectrum of (b) [Zn(bpy)3](CrO4)0.5NO3.65H2O (Ccc2), and (c) [Cu(H2O)(bpy)2]2[HfF6]2.3H2O (Pna21).

Studying the role of defects in lepidocrocite nanorods

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Iron oxide nanoparticles are interesting from both the fundamental and applied viewpoints due to their magnetic behaviour. Recently, it has been found that depending on the synthesis conditions Fe$_{3-x}$O$_4$ nanoparticles can exhibit so-called anomalous magnetic properties such as reduced saturation magnetization compared to bulk values, emergence of exchange-coupling effect, etc.; due to the presence of defects$^1$. The presence of defects can thus be also of importance for other types of iron (oxy)hydroxides. In this work we investigate the presence of defects in lepidocrocite ($\gamma$-FeOOH) nanorods (average dimensions of 250 × 10 × 10 nm$^3$) using electron microscopy and x-ray diffraction. Also, the magnetic properties of the materials have been measured with vibrating sample magnetometry (VSM).

From high resolution TEM data we observed clearly the presence of dislocations in the (020), (004) and (-110) planes of the structure. The corresponding Burgers vectors (magnitude and direction of the lattice distortion) are $\frac{1}{2}$ <010>, $\frac{1}{4}$ <001> and $\frac{1}{2}$ <-110>, respectively. From GPA analysis we saw that deformation of (020) lattice fringes is rather uniform (± 5 %) and lattice distortion along deformation profile line can be ascribed to dislocations. Negative deformation corresponds to the shorter lattice parameter. The diffuse intensity, which can be related to defects (dislocations, anti-phase boundaries, etc.), was detected along <010> direction from electron diffraction patterns. Rietveld refinement of PXRD pattern using Popa algorithm shows an enhanced strain on (002) and (022) planes. Moreover, the magnetic characterization indicates the presence of a ferrimagnetic component in antiferromagnetic lepidocrocite and exchange bias at low temperatures.

Force field prediction of a reversal transition in molecular crystals

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Polarity formation is a general growth feature of systems showing unidirectional self-assembly of polar building blocks into a bulk state1. Channel-type inclusion compounds, single component molecular crystals, solid solutions, optically anomalous crystals, inorganic ionic crystals, biological tissues and biomimetic composites investigated experimentally all showed domains of opposite polarities in their final grown state2.

In this field, molecular crystals made of dipolar organic molecules growing into a polar crystals structure are subject to undergo a reversal transition and open up fascinating opportunities for computational and experimental studies. In the frame of a general theory on stochastic polarity formation, the analytical description demonstrates that the reversal will take place in that direction (sectors involving the polar axis) where $180^\circ$ orientational defect formation is less endothermic3. Therefore, force field calculations of the energy of $180^\circ$ defect formation at both types of faces, i.e $(hkl)$ and $(\overline{h} \overline{k} \overline{l})$ may allow to predict which side of the polar axis should show reversal of most of the dipoles.

This basic property of molecular crystals is exemplified by investigating real systems for which at first we describe the structures and the representative $(hkl)$, $(\overline{h} \overline{k} \overline{l})$ faces for which interaction energies are explicitly calculated by taking into account the specific symmetry of the lattice. Conceptually a quite simple procedure, the practical elaboration can be rather complicated, because of the presence of different sites which are symmetry independent at the surfaces of different $(hkl)$ faces.

The two chosen dipolar molecules are 1-chloro-4-nitrobenzonitrile and 1-bromo-4-cyanobenzonitrile. The molecules were selected as such to provide geometries and sizes which do not impose a significant surface site reconstruction (relaxation), when an $180^\circ$ reversed attachment is considered.

We will present the results of a structural and energetical analysis involving different faces where we may define a difference of energy when docking a molecule down or up, by looking at the values of this energy difference predictive for the polar behaviour of individual faces.

This configurational study highlights a relationship between the symmetry of a surface and the reversal transition which may occur when growth proceeds.

Rietveld refinement of XRD-CT data

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The main aim of solid catalyst study is to understand the relation between catalyst structure and its function. The analysis of solid catalyst structure under operando conditions can provide the user with essential information about the catalyst active sites1.

X-ray Diffraction Computed Tomography (XRD-CT) allows for imaging the interior of a catalyst, simultaneously providing the information about its chemical composition. When combined with a bright X-ray beam and state-of-the-art detectors with a fast data acquisition/data readout, this technique can be applied to study the three-dimensional structure of catalysts, under operating conditions2.

When analysing a diffraction pattern of a crystalline material containing several phases, one may find difficulties in the phase identification, due to the peak overlap. Therefore, the Rietveld refinement should be performed, aiming to refine the model structure of the catalyst, created by the user. In addition, for each phase presented in the model, useful information regarding the lattice parameter, crystallite size or finally percentage composition can be extracted. However, analysing diffraction patterns as a function of an external variable, such as temperature or pressure, leads to better understanding of the behaviour of the system under investigation. This approach, called parametric refinement, in comparison with single or sequential refinement, results in higher precision of refined parameters and greater stability of refinement process3. In addition, it offers a possibility to refine the non-crystallographic factors, such as temperature, which can be useful when treating the space resolved data, where the possibility of hot-spots formation is possible.

In this study, a La-Sr/CaO catalyst, used in OCM process (Oxidative Coupling of Methane) was studied in a packed-bed reactor. The catalyst was firstly placed in the atmosphere of neutral gas during the temperature ramp (from room temperature to 780 °C) and then in the mixture of methane and oxygen, with different methane to oxygen ratio. The XRD-CT analyses were performed at the station ID31 of ESRF in Grenoble, using a monochromatic X-ray beam of 70keV. The data was refined using software Topas 5 and MATLAB.

This study aims to present the approach of parametric refinement of XRD-CT data and to demonstrate the applied methodology using the obtained preliminary results to explain it.

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Reference:
Formation of porous coordination polymers using zinc-nitrile interaction

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Soluble host-guest coordination networks have many potential applications, such as selective guest removal, and detection.\textsuperscript{1} Here we present new coordination polymers based on zinc-nitrile interaction. Porphyrin core was used as a template and its periphery was functionalized with 4-cyanophenyl groups in \textit{trans} fashion at two meso positions. Noncompeting aryl groups are situated at remaining other two meso positions. Through zinc-nitrile interactions it forms $4 \times 4$-networks and forms a layered structure. By changing aryl groups it is possible to change size and electronic environment of the spaces between the layers. Thus, these kinds of coordination polymers can be used for selective guest inclusion.\textsuperscript{2}

The use of supramolecular chemistry concepts to design and assemble novel molecular arrangements

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In order to improve crystal quality and size for magnetic measurements, Dy(III)Cl₃ and Er(III)Cl₃ react with di-2-pyridyl ketone (dpk) and pyrazole to give metal complexes Dy₃Cl₃L’₃L”₂ (1) and Er₃Cl₃L’₃L”₂ (2) in which L’ = py₂C(OH)O⁻ and L”’ = py₂(C₃H₃N₂)CO⁻.

The crystal structures of (1) and (2) have been determined by X-ray diffraction. (1) crystallises in the rhombohedral space group R-3 with Z=18, a= 37.901(3), b= 37.901(3), c= 30.9794(19) Å. (2) crystallises in the rhombohedral space group R-3 with Z=18, a= 37.7853(14), b= 37.7853(14), c= 30.8449(8) Å.

Supermolecular interaction of Manganese Schiff base complexes.

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Transition metal Schiff base complexes continue to be the subject of extensive research because of their catalytic roles, which includes Jacobsen catalyst, Photo system II models and water photo-oxidation catalysts and hydrogen peroxide activators, so that a lot of research has been directed towards modifying the stereochemistry around the metal centre.

An interesting feature of these complexes is their ability to dimerise into bimetallic catalytic cores. Unpublished work carried out at Manchester shows carboxylate capped, Mn(III) Schiff base monomers associating into dimers via π-π interactions, and, in the same crystal structure, dimers in which the complexes are linked via phenoxy bridges, thus demonstrating an exquisite balance between the two forms of association.

The proposed research will look at the supramolecular interactions of Schiff-base monomers, starting with the above complex, which will be studied to examine if dimer formation has temperature dependence.
Can we predict the jumping of crystals? The case of oxitropium salts.

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Some crystals jump during the phase transition. These thermosalient crystals are biomimetic, nonpolymeric self-actuators par excellence. Yet, due to exclusivity and individuality of the phenomenon, all present investigations have not yet resulted in the full elucidation of this mechanism, let alone enabled us to predict necessary prerequisites for its existence so we aimed our research towards new materials obtained by careful modification of compounds in which the effect was noticed. It is to be expected that this exotic and unexpected effect will be extremely sensitive to subtle changes in the chemical composition (change of the anion, change of the functional groups, change of the position of the functional group inside the aromatic ring) and these investigations will enable determination of necessary chemical/structural parameters so as to arise the thermosalient effect in the system. No matter if these compounds will be thermosalient in nature, or not, comparison between original systems and their derivatives will certainly provide new and helpful insight into elucidation of thermosalient behavior and offer new guidelines in the sense of targeted fabrication of new thermosalient materials.

One of the first systematic studies of this fascinating effect, which paved a way towards its final elucidation, was conducted on the anticholinergic agent oxitropium bromide.2 It was shown that the unit-cell distortion is accompanied by a conformational change of the oxitropium cation, which triggers increased separation between the ion pairs in the lattice at nearly identical separation between the cation and the anion within each ion pair. At the molecular level, the cation acts as a molecular shuttle composed of two rigid parts (epoxy-aza-tricyclic-nonyl portion and phenyl ring) that are bridged by a flexible ester linkage. The structure of the rigid, inert aza-tricyclic portion remains practically unaffected by the temperature, suggesting a mechanism in which the large, thermally accumulated strain is transferred over the ester bridge to the phenyl ring, which rotates to trigger the phase transition.

In an attempt aimed at the targeted fabrication of thermosalient materials, a series of oxitropium salts was prepared. Oxitropium bromide was used as a starting reagent for preparation of several other oxitropium salts. Precursor compound was dissolved in minimal amount of water and the appropriate lead(II) salt was added under stirring conditions. After period of 1 h lead(II) bromide, which precipitated during the stirring, was removed by filtration. One of the prepared systems, oxitropium nitrate, showed thermosalient behaviour during observation on the hot-stage microscope and exhibited joyful jumps during heating (around 134ºC) and cooling (around 98ºC). Detailed structural (high temperature in-situ XRPD), thermal (DSC and TGA), spectroscopic (FT-IR), mechanistic and theoretical (DFT using state-of-the-art nonempirical vdW-DF-cx functional) study was conducted which revealed much information about the thermosalient effect in this system which are necessary to reach the final goal of understanding the nature and mechanism of this fascinating phenomenon.

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References

The role of amino acids as simple models of organic matrix molecules participating in calcium carbonate biomineralization

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Calcium carbonate is the main inorganic component of biominerals in a wide range of invertebrate organisms and is present either as a specific polymorph (calcite or aragonite), hydrated or in an amorphous form. The calcite skeletal elements regularly contain small amounts of proteins which are either incorporated or adsorbed on the single crystals of calcite. Previously it has been shown that isolated fragments of proteins extracted from mineralised tissue, or their synthetic macromolecular analogues, exert a significant influence on the morphology and crystal structure of calcium carbonate when precipitated in the appropriate model systems.1-3 In addition, it is known that the in vitro formation of specific crystal modifications is typically determined by parameters such as temperature or initial supersaturation, as well as by the presence of inorganic or organic additives.

The aim of this research is to investigate polymorphism and crystallographic distortions of the calcite lattice due to the influence of amino acids, selected as simple models of biomacromolecules supposed to be responsible for nucleation, growth and transformation of calcium carbonates in biomineralising systems. For that purpose amino acids having distinct chemical and physical properties were selected: asparagine (Asn), aspartic acid (Asp) and lysine (Lys) were chosen because of differently charged side chains, while tyrosine (Tyr) and phenylalanine (Phe), as well as serine (Ser) and alanine (Ala) have different polarity. The results of structural (FT-IR, PXRD, EPR)4 and morphological (SEM) analyses indicated an overall inhibition of calcite precipitation in the presence of all amino acids. The inhibition is probably caused by a slower transformation of initially formed vaterite into the calcite.5 Since the selected amino acids are charged under the applied experimental conditions, some surface interactions are assumed to be responsible for the observed effect.

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The influence of fluorinated phosphine’s on [XAuPR$_3$] structures

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A series of gold(I) complexes of the type [AuX{PR$_3$}] (where R = (m- FC$_6$H$_4$), (3,4,5-F$_3$C$_6$H$_2$), (3,5-(CF$_3$)$_2$C$_6$H$_3$), (Ph$_2$(C$_6$F$_5$), and X=Cl, Br, I) have been prepared and structurally characterised by single crystal X-ray diffraction in order to investigate the presence of short Au···Au (aurophilic) interactions. Gold-Gold distances ranging from 3.1273(8) Å to 9.0059(6) Å were observed. It is found that the presence of shorter Au···Au distances coincides with more acute X-Au-P angles, whilst the complexes that exhibit more linear geometry show longer Au···Au distances. While some of these complexes showed short intramolecular F-F distances and hydrogen bonding.
Spatially resolved X-ray diffraction of Moso bamboo reveals tissue-specific microfibril angle distribution

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Bamboo is a plant known for its exceptionally fast growth. Moso bamboo (Phyllostachys pubescens Mazel) is commercially the most important Chinese bamboo species and it is used as a construction material for houses, scaffolding, furniture and other objects. The bamboo culm tissue is a composite structure of vascular bundles embedded in a parenchyma cell matrix. In order to study the cellulose microfibril angle (MFA) distribution of these two components, a set-up combining X-ray diffraction (XRD) and microtomography is used (Fig. 1).

With conventional, non-localized, XRD only the average scattering pattern (Fig. 1b) could be measured and the contribution of the different tissue types cannot be resolved. With the spatially resolved XRD, enabled by the combined tomography set-up, regions-of-interest can be selected from the tomographic reconstruction slice and measured using the 200-µm wide monochromatic beam.

The tissue-selective XRD patterns show that the parenchyma cells (Fig. 1c) have weak preferred orientation whereas the vascular bundles have strong preferred orientation (Fig. 1d). The MFA distributions are compared for these two tissue types and for inner and outer parts of the bamboo culm wall.

Figure 1: (a) Tomographic reconstruction slice of the Moso bamboo sample. The arrows indicate where the X-ray diffraction patterns shown in b-d were measured.
(b-d) Corresponding X-ray diffraction patterns. The 200-reflection of cellulose (marked with an arrow) is used to determine the microfibril angle distribution.

3D Grain mapping for continuous neutron sources

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Polycrystalline materials undergoing thermal or mechanical loading suffer deformations and damage which can modify their grain size, orientation and texture.

To obtain multigrain information from crystalline samples, 3D grain mapping is performed using x-rays at synchrotron radiation sources.1,2 However, the scope of this technique is limited due to the lack of penetration power inside of bulky metallic samples. S. Peetermans previously demonstrated the feasibility of such technique applied to neutrons.3

Peetermans acquired the data at the ICON beamline using two imaging detectors: one in transmission mode and one in backscattering mode. In order to avoid spot overlap from different grains, the diffraction data was acquired with a pink beam of 4.3Å and then 3.7Å. Because Friedel pairs were used to identify the grain position, every spot had to be coupled with its pair at 180° rotation so the sample had to be rotated 360°. This experiment provided a 3D reconstruction of 12 grains from an aluminum sample. We believe the same information could be obtained with a more robust and time-efficient method.

Using white beam illumination we plan to obtain spots from all the Bragg planes at the same time, and solve the spot overlap using image processing tools. Once the spots are segmented we can do without the Friedel pair matching by using a forward model to index the grains so that only a 90 degrees rotation is required.4 With this new method we aim to reduce the acquisition time of the diffraction data by a factor of 8, and index a larger number of grains.

Some of the scientific cases for this technique are shape memory alloys, metallic samples from additive manufacturing, meteorites and other coarse grain samples.

High Pressure X-Ray Diffraction of the Paramagnetic Compound UPd$_2$Sn

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Compounds of the form AnPd$_2$Sn (An= Th, U, Np, and Pu) crystallize in an orthorhombic distortion of the FCC Heusler lattice. Though they are isostructural, UPd$_2$Sn presents very different magnetic behavior from its transuranic counterparts. Both NpPd$_2$Sn and PuPd$_2$Sn order antiferromagnetically, but UPd$_2$Sn remains paramagnetic down to at least 80 mK, even though neutron scattering measurements show clear signs of magnetic coupling. However, reducing its Pd content by only 3% removes the orthorhombic distortion and causes an antiferromagnetic transition at 25 K.

We report here high-pressure X-ray diffraction studies of the paramagnetic compound UPd$_2$Sn, as well as new resistivity, magnetic susceptibility, and heat capacity measurements for comparison to other AnPd$_2$Sn-type compounds. A polycrystalline sample of UPd$_2$Sn was prepared by arc-melting and loaded in a diamond anvil cell. Its crystal structure was refined from powder X-ray data and showed an orthorhombic symmetry with Pnma space group and a= 9.956(4)Å, b= 4.601(2)Å and c= 6.874(3)Å cell parameters at room temperature and pressure. Patterns were taken at regular intervals up to 40 GPa, showing that the orthorhombic structure remains up to the highest pressure, with no sign of the FCC structure. Fits to a Birch-Vinet equation of state gave a value of $B_0 = 187.28$ GPa for the Bulk Modulus. The resistivity, magnetic susceptibility, and heat capacity data confirm UPd$_2$Sn as a paramagnetic, non-superconducting, heavy fermion system. This sets it apart from both the Np and Pu compounds, as well as its non-magnetic analogue ThPd$_2$Sn.

Binary and Ternary Cu(II), Mn(II), VO(II) and Fe(III) Complexes of Doxycycline with Polypyridyl Ligands: Synthesis, Characterization and Biological Applications

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The pleiotropic properties of tetracyclines, the biological applications of transition metals, the improved biological activities of tetracyclines upon chelation by metal ions as well as the biological importance of polypyridyl ligands have prompted us to synthesize some binary and ternary transition metal complexes of the antibiotic doxycycline with polypyridyl ligands. Binary and ternary complexes of copper (II), manganese (II), iron (III) and oxovanadium (II) with doxycycline and polypyridyl ligands were synthesized and well characterized in solid state and in solution by UV-Vis, FT-IR, EPR and ESI-MS.

X-ray crystal structures of complex Cu(II)-doxycycline complexes 2 and 3 confirms that out of several binding sites doxycycline coordinates through the amide oxygen and the keto oxygen of ring A. Complexes 3, 4 and 5 exhibit nearly similar and moderate DNA binding constants reflecting groove binding. All copper complexes cleave pBR322 DNA by oxidative mechanism at significantly low concentration. Further these complexes act as MMP inhibitors similar to doxycycline. Complexes are cytotoxic towards MCF-7 cell line, complex 4 being the most potent while the complexes are more active than the chloroquine diphosphate and the drug Artesunate against CQ-resistant parasites P. falciparum Dd2 strain.

Doxycycline complexes with manganese (II), iron (III) and oxovanadium (II) were tested for their antimicrobial activities against pathogenic as well as chloroquine-sensitive and chloroquine-resistant P. Falciparum. In all cases, the complexes are more potent than doxycycline, the parent antibiotic from which they were synthesized while some are more active than the chloroquine diphosphate and the drug Artesunate against CQ-resistant parasites P. falciparum Dd2 strain. The antibacterial activities of some of these complexes are comparable and in some cases higher than that of doxycycline.

The cytotoxicity experiments of the copper complexes show that they can also be considered as potential anticancer agents and are effective as Matrix Metalloproteinase (MMP-2) inhibitors.