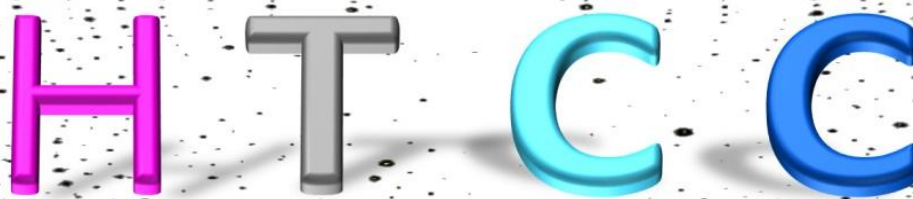


Hot Topics in Contemporary Crystallography



Programme book

22-26 April, 2017, Poreč, Croatia

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Crystallography

	Saturday 22 nd April 2017	Sunday 23 rd April 2017	Monday 24 th April 2017	Tuesday 25 th April 2017	Wednesday 26 th April 2017
8:30 - 9:30	Arrival		S. Parsons (chair: A. Šantić)	P. Macchi (chair: M. Đaković)	Departure
9:30 – 10:30		S. Hasnain (chair: A. Višnjevac)			
10:30 - 11:00		Coffee break			
11:00 - 13:00	H. Chapman (chair: B. Kojić-Prodić)	M. Adam (chair: J. Popović)	C. Jelsch (chair: I. Sabljjić)		
			K. Molčanov (chair: I. Sabljjić)		
13:00 - 15:00	Lunch break (Lunch is served: 12:00 – 14:00)				
15:00 - 17:00	Registration	I. Schlichting (chair: B. Kojić-Prodić)	S. Parsons (chair: A. Šantić)	P. Macchi (chair: M. Đaković)	
				S. Hasnain Concluding remarks	
17:00 - 17:30	Coffee break				
17:30 - 19:00	Opening ceremony	M. Müller (chair: Z. Štefanić)	M. Adam (chair: J. Popović)	Poreč guided tour	
19:00 – 21:00	Dinner			Farewell dinner	

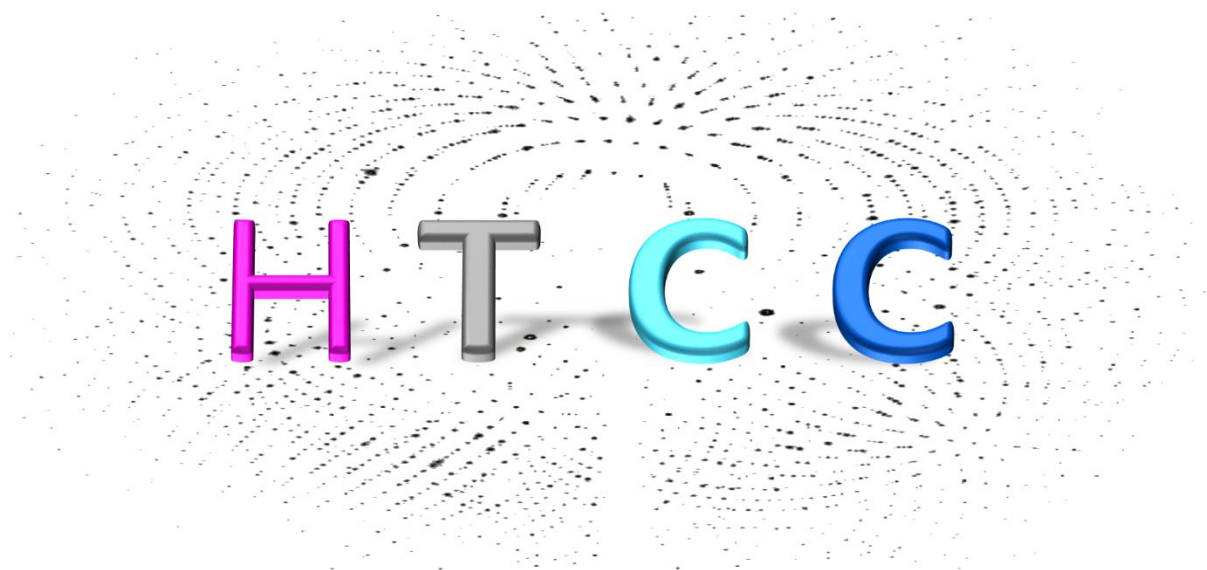
Saturday (22nd April 2017)

15:00 – 17:30 Registration

Registration will take place in front of the *Magnolia Hall of the Valamar Diamant Hotel*.

17:30 – 19:00 Opening ceremony

Opening ceremony will take place in Magnolia Hall, Valamar Diamant Hotel



Hot Topics in Contemporary Crystallography

Poreč, Croatia, Apr. 22nd to 26th, 2017

Opening ceremony

Valamar Diamant Hotel, Magnolia Hall, Apr. 22nd, 2017, 17:30 PM

- 17:30 *Ana Šantić*: Welcome to HTCC2
- 17:35 *Aleksandar Višnjevac*: Croatian Association of Crystallographers – five years of a tireless service to the Croatian crystallographic community
- 17:45 *Biserka Kojić-Prodić*: HTCC – idea and objectives
- 17:55 *Bruker AXS / Aparatura d.o.o representative*: A word from the main sponsor
- 18:05 *Ana Šantić*: House-keeping remarks and invitation to the welcome cocktail

Sunday (23rd April 2017)

09:30 – 10:30 **Samar S. Hasnain** - Introductory talk

Conventional protein crystallography vs dynamical crystallography based on synchrotron and X-ray free electron laser sources

I am going to review a project that was initiated in our laboratory in 1992, quarter of a century ago. It is an enzyme system that uses a coupled redox system that are linked by neighbouring residues. Using conventional crystallography with point mutations, fast kinetics and on-line spectroscopies we have established the gating of the two redox centres and the delivery of substrate and utilisation. Serial crystallography using controlled radiation dose from a microfocus SR X-ray beam and fast detectors we have obtained structural movies of the conversion of substrate to product and its release concomitant with the recycling of the substrate binding site to resting state. Femtoseconds crystallography from SACLA has provided structural evidence rationalising an alternative role of the catalytic site that has remained unexplored for 30 years despite many groups working on related enzyme systems.

11:00 – 13:00 **Henry Chapman**

Time-resolved macromolecular structure determination using XFELs

X-ray free-electron lasers have opened up exciting new opportunities for the determination of macromolecular structures at physiological temperatures and conditions. The pulses, of only femtoseconds duration, give rise to measurements that out-run the processes of radiation damage and allow us to carry out protein crystallography of transient structures at a correspondingly high temporal resolution. The high intensities also open up new methods for phasing diffraction and to extend techniques to objects that are difficult to crystallise.

15:00 – 17:00 **Ilme Schlichting**

Protein structure and dynamics using X-ray free-electron lasers

Protein crystallography using synchrotron radiation sources has had tremendous impact on biology, having yielded the structures of thousands of proteins and given detailed insight into their working mechanisms. However, the technique is limited by the requirement for macroscopic crystals, which can be difficult to obtain, as well as by the often severe radiation damage caused in diffraction experiments, in particular when using tiny crystals. To slow radiation damage, data collection is typically performed at cryogenic temperatures. The femtosecond X-ray pulses provided by X-ray free-electron lasers (FELs) allow the acquisition of high resolution diffraction data from micron-sized macromolecular crystals at room temperature beyond the limitations of radiation damage imposed by conventional X-ray sources. Moreover, the short duration of the pulses enable time-resolved studies at the chemical time-scale of femtoseconds. The novel sources require new approaches for sample preparation, delivery, data collection and analysis. These approaches as well as recent results obtained will be presented.

17:30 – 19:00 **Marcus Müller**

Hybrid Photon counting detectors for short-wavelength crystallography

The past ten years have seen tremendous advances and progress in X-ray detector technology available for crystallography. Hybrid Photon Counting (HPC) detectors have brought crystallography the advantages of single-photon counting and direct detection in a solid-state sensor. The absence of readout noise and detector dark signal ensure high data quality irrespective of exposure time or number of acquired frames; a digital counter in each pixel enables highest dynamic range and allows the collection of low- and high-resolution data simultaneously. Direct detection of X-rays in solid-state sensors provides a small, sharp point-spread function, a critical advantage for accurately measuring closely spaced reflections or diffuse scattering. Last but not least, direct detection with CdTe as a sensor material provides more than 90% quantum efficiency and makes best use of the precious photons from high-energy sources. In summary, Hybrid Photon Counting (HPC) detectors have the potential to move extremely challenging short-wavelength data acquisition from the synchrotron to the home lab.

This presentation will give an overview of how HPC technology works and why it provides a number of unique advantages. Results from the experimental characterization of detector properties such as quantum efficiency, point-spread function, and count rate capability of the PILATUS3 CdTe detectors will be presented. Furthermore, some highlights from synchrotron and laboratory diffraction experiments will demonstrate how HPC detectors facilitate contemporary crystallography.

08:30 – 10:30 **Simon Parsons** (Introductory talk)

High pressure crystallography: practical aspects

Pressure is amongst the most powerful tools for manipulating energy landscapes in molecular crystal structures. This talk will focus on practical methods of high-pressure crystal structure determination. Methods for generating and measuring high pressure will be described, along with procedures for mounting samples and for growing them in situ under pressure. The stages of data collection, reduction, solution and refinement all need to be modified to account for the limitations imposed by high-pressure devices. Use of both X-rays and neutrons will be discussed, along with the role theory and other experimental techniques can play in helping to understand the effect that pressure has on a system.

11:00 – 13:00 **Martin Adam**

Non-ambient X-ray diffraction– learn more about your sample

Synthesis of ceramics through sintering at elevated temperatures under controlled atmosphere, steel hardening through annealing steps, humidity and temperature effects on the stability of pharmaceutical compounds – detailed knowledge of what happens to a sample at non-ambient conditions is essential for research, process optimization, and quality control. Lifetime and capacity optimization of batteries is another topic receiving a lot of attention today. The answer on all these matters can be found investigating the formation of new phases, changes in microstructure, or optimization of stress and texture properties which makes X-ray diffraction the preferred method to gather that knowledge. Our X-ray diffractometers, D8 ADVANCE and D8 DISCOVER for XRD as well as D8 QUEST and D8 VENTURE for SC-XRD, enable fast data acquisition to efficiently study kinetics and thermodynamics at non-ambient conditions. Today, dedicated sample stages to study the effects of temperature, atmosphere, humidity or pressure are available, fully software integrated, and easy to use. Selected examples will be presented with a focus given to temperature dependent measurements as these are receiving by far the most interest.

15:00 – 17:00 **Simon Parsons**

The effect of high pressure on molecular materials

The effect of pressure on a number of different classes of molecular crystal structures has been investigated, including very simple compounds such as acetone and pyridine, ligands used in metal extraction, amino acids and metal complexes. Work in the organic solid state has largely focussed on phase transitions, and efforts to understand the competing factors which control these transitions will be described. Intramolecular bond distances and angles are usually not greatly affected in organic solids, but the same is not true in coordination complexes, where metal geometry is much more flexible. The talk will also describe how this feature makes high-pressure an extremely useful tool for exploring structure-property relationship in coordination materials.

17:30 – 19:00 **Martin Adam**

How to Build Cutting Edge Solutions for In-house Single-Crystal X-ray Diffraction?

Today's Single Crystal X-ray Diffraction (SCD, SC-XRD) systems greatly benefit from a number of recent game changing developments. This holds for the X-ray source and optics, for the goniometer and low temperature devices, but even more for newly developed software and detectors. All-aircooled solutions have set new standards in low-power consumption and reliability while at the same time enabling the analysis of ever smaller, more challenging samples.

To a large extent this can be attributed to microfocus technology and modern multilayer Montel optics providing an X-ray intensity seen at synchrotrons not too long ago. Systems using Liquid metal jet sources deliver data sets of a quality which can compete with current state-of-the-art synchrotron installations. A keystone to the success are large active area CPAD detectors with high Detective Quantum Efficiency (DQE). Last but not least, modern software packages allow data processing of challenging samples for the expert user but offer also offer a high level of automation to novices and occasional users. This presentation will focus on technical details of modern in-house instrumentation and discuss the pro's and con's for various applications.

08:30 – 10:00 **Piero Macchi** (Introductory talk)

Charge density studies of compounds at high pressure

In this talk, the necessities and pitfalls of experimental determination of the electron density in crystals under high pressure are discussed. Results on some test system as well as from more intriguing species will be discussed.

11:00 – 12:00 **Christian Jelsch**

Practical aspects of X-ray electron density analysis and application to proteins and molecular interactions

Latest tools for the multipolar refinement and analysis of charge density at ultra-high resolution will be described. The methodology has been extended from small molecules to biological macromolecules like protein/ligand complexes through the use of electron density databases.

The impact of multipolar charge density on molecular interactions, notably hydrogen bonds, will be discussed. The driving forces in crystal packing formation can be revealed by Hirshfeld surface analysis.

12:00 – 13:00 **Krešimir Molčanov**

Structure properties relationship derived from X-ray charge density: Unusual chemical bonds bordering intra-and intermolecular contacts

Application of X-ray charge density to study of interesting chemical problems is illustrated on several examples involving electron delocalisation and charge transfer. Semiquinone radicals are stabilised by delocalisation of the unpaired electron and negative charge, and their electron structure is somewhere between aromatic (fully delocalised π electrons) and quinoid (distinguishable single and double bonds). In the solid state they form extended π -stacks, and the spin coupling can be diamagnetic (high electron density between the rings) or antiferromagnetic (low electron density between the rings). The border line between a weak covalent bond and a strong intermolecular interaction (such as a hydrogen or a halogen bond) is often a fuzzy one, and the borderline cases are illustrated on an $\text{H}_2\text{O}-\text{H}-\text{OH}_2$ fragment (Zundel ion) and $\text{N}-\text{Br}-\text{N}$ fragment.

15:00 – 16:00 **Piero Macchi**

Materials properties from electron density

The electron density distribution determines some properties of a material, especially connected with the electrostatic moments and the energy. By means of perturbation theory one may also derived additional properties, such as the dielectric ones.

16:00 – 17:00 **Samar S. Hasnain** (Concluding Remarks)

How advances in science and technology have reinforced each other for expanding universe of crystallography?

X-ray Crystallography was established just over 100 years ago through the pioneering efforts of Max von Laue, Lawrence Bragg and Charles Golver Barkla who each received a Noble prize in 1914, 1915 and 1917, respectively. Lawrence Bragg shared the prize with his father William Bragg who was only persuaded by Laue's experiments and Lawrence Bragg's explanation that Röntgen rays were photons of wavelengths comparable to interatomic spacing and that they were not a 'new' particle making up an atom. The power of X-ray crystallography became obvious in the second quarter of the last century providing the vision for the establishment of the International Union of Crystallography in 1947, marking crystallography as a mainstream science activity which had the capabilities of impacting all sciences. The advances in computers and demands for higher intensities led to major growth in the last quarter of the last century leading visionaries to contemplate structure determination of complex biological systems without the 'tyranny' of crystals. Though X-rays have not yet realised this dream, last five years have seen a major transformation in cryoEM¹, which I have called 'method of the decade'². It has already brought many high resolution structures of medium sized systems. I will cover some of these developments in my talk.

Posters

- P01** – M. Hinterstein: Correlation of crystal structure with macroscopic properties in electroceramics
- P02** – M. Jurić: From discrete or polymeric heterometallic complexes to the mixed-metal oxides
- P03** – R. Katava: Synthesis and supramolecular solid state structure of dioxovanadium(V) complexes with 2-benzothiazolylhydrazone ligands
- P04** – Kofoed: The discovery of a natural occurring NASICON phase, $\text{NaMgAl}(\text{SO}_4)_3$
- P05** – M. Lozinšek: Extending the chemistry of krypton
- P06** – E. A. Lukina: Hydration and dehydration of saranchinaite
- P07** – F. Marlton: Uncovering phase boundaries in ternary piezoelectric ceramics
- P08** – V. Milašinović: A partial charge transfer between iodide ions and quinoid rings
- P09** – E. Peresyphkina: Four in ten millions: isomers of intrinsically vacant supramolecule
- P10** – N. A. Tumanova: Topotactic formation of new high-pressure polymorph of L-alanine via methanol-water solvate
- P11** – N. Tumanova: Opening pandora's box: chirality, polymorphism, and stoichiometric diversity in flurbiprofen/proline cocrystals
- P12** – A. Virovets: Giant pentaphosphaferrocene-based supramolecules as molecular containers
- P13** – V. Zvoníček: Rational approach towards Ibrutinib solvates

Correlation of crystal structure with macroscopic properties in electroceramics

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Keywords: neutron, piezoceramics, texture, electric field

Piezoelectric ceramics exhibit the remarkable property to couple elastic strain and polarization under the influence of an applied electric field. Among the various types of piezoelectric devices, especially actuators rely on high electric fields to generate high strains and forces. Prominent examples for actuators are multilayer stack actuators used for nanopositioning or in modern combustion engines for automobiles to control injection cycles. The two most important characteristics of this class of materials are macroscopic strain and piezoelectric coefficient. Despite extensive studies and elaborated measurement techniques, the correlation between macroscopic strain and structural response is still not fully understood.

Most of the relevant systems found up to now are compositions close to phase boundaries linking highly correlated phases. This results in major challenges for structural analyses due to overlapping reflections. Apart from the well-known field induced structural responses such as domain switching and the converse piezoelectric effect, we recently identified field induced phase transformations in different systems as an additional poling mechanism [1,2]. In order to resolve all three involved poling mechanisms within only one experiment we developed a structural analysis technique with in situ X-ray and neutron powder diffraction data [3], using the program MAUD [4]. The results not only separately reveal the contributions of each poling mechanism to the macroscopic strain, but also different behaviours of the individual phases. The calculation of the elastic strain perfectly matches the macroscopic observations, confirming the accuracy of the applied models. Since this method yields fundamental information such as the crystal structure as a function of applied electric field, we were able to calculate the piezoelectric coefficient for the individual phases based on information on the atomic scale. In this contribution we present the latest research on the elucidation of strain mechanisms and fundamental properties in piezoceramics.

- [1] M. Hinterstein, M. Knapp, M. Hoelzel, W. Jo, A. Cervellino, H. Ehrenberg and H. Fuess, *J. Appl. Phys.* 43, 1314 (2010).
- [2] M. Hinterstein, J. Rouquette, J. Haines, Ph. Papet, M. Knapp, J. Glaum and H. Fuess, *Phys. Rev. Lett.* 107, 077602 (2011).
- [3] M. Hinterstein, M. Hoelzel, J. Rouquette, J. Haines, J. Glaum, H. Kungl, M. Hoffman, *Acta Mater.* 94, 319-327 (2015).
- [4] L. Cont, D. Chateigner, L. Lutterotti, J. Ricote, M. L. Calzada, J. Mendiola, *Ferroelectrics* 267, 323 (2002).

From discrete or polymeric heterometallic complexes to the mixed-metal oxides

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Mixed-metal oxides are an important class of advanced materials, due to their stability, low cost, low toxicity, useful photophysical properties and wide range of technological applications. They are mostly utilized as catalysts and structural ceramics, but recently, the use of mixed-metal oxides as sensors, actuators, and smart materials has also been explored. It is known that the effect of crystallinity, particle size, structure and morphology of these materials could highly affect their properties.

The possibility of using coordination polymers through the thermal decomposition process as molecular precursors in the synthesis of nanomaterials with high surface and specific morphology has been considered only recently. This method of obtaining oxide materials, compared with conventional methods, has several advantages: (i) the obtained material is more homogeneous because the metals are mixed at the molecular level; (ii) the resulting materials have relatively high specific surface areas because the crystalline oxides are formed under significantly milder conditions than those in, for instance, solid-state reaction processes; (iii) the existence of bridging or chelating ligands in the precursors prevents metal separation during oxide formation; (iv) there is much greater control of the metal stoichiometry in the final oxide. The $\text{C}_2\text{O}_4^{2-}$ group easily decomposes to gaseous CO_2 and CO at low temperatures, and hence, the oxalate-based solids can serve as a convenient source of oxides [1].

Utilizing the preparation of the oxide materials *via* thermal decomposition, several oxalate-based compounds were tested as molecular precursors. Discrete heterotetranuclear oxo-bridged compound $[\text{Cr}_2(\text{bpy})_4(\mu\text{-O})_4\text{Nb}_2(\text{C}_2\text{O}_4)_4]\cdot 3\text{H}_2\text{O}$ (**1**; bpy = 2,2'-bipyridine) showed to be a good candidate for molecular precursor-to-material conversion, yielding the rutile-type CrNbO_4 oxide after heat treatment at 900°C . The thermal processing of heterodimetallic one-dimensional (1D) compound $\{[\text{CaCr}_2(\text{bpy})_2(\text{C}_2\text{O}_4)_4]\cdot 0.83\text{H}_2\text{O}\}_n$ (**2**) proved to be a simple, one-step synthesis route for the preparation of the $\beta\text{-CaCr}_2\text{O}_4$ phase at 1100°C in nitrogen flow. The r.t. structure of $\beta\text{-CaCr}_2\text{O}_4$ is isomorphic with calcium ferrite, unlike most chromate structures, which usually crystallize as spinel oxides. A three-dimensional (3D) oxalate-based coordination polymer $\{[\text{Co}(\text{bpy})_3][\text{Mn}_2(\text{C}_2\text{O}_4)_3]\cdot \text{H}_2\text{O}\}_n$ (**3**) was used as a single-source precursor for the formation of spinel oxide CoMn_2O_4 heating at 800°C . Magnetic properties of mixed metal oxides prepared *via* thermal decomposition of **1–3** have been studied in detail.

- [1] M. Jurić, J. Popović, A. Šantić, K. Molčanov, N. Brničević and P. Planinić, *Inorg. Chem.* **52** (2013) 1832–1842.

Synthesis and supramolecular solid state structure of dioxovanadium(V) complexes with 2-benzothiazolyhydrazone ligands

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Dioxovanadium(V) complexes and 2-benzothiazolyhydrazones both present promising area of research with various biological applications. Combining them in a unique system could enhance their biological activities. In order to increase solubility of complexes in water medium ionic dioxovanadium(V) complexes with 2-benzothiazolyhydrazone ligands were prepared.

Reactions of 2-hydrazinobenzothiazole and aromatic aldehydes afforded Schiff base ligands (H_2L^{1-3}). Reactions of $[V^{VO}(acac)_2]$ with H_2L^{1-3} in ethanol solution and with the equimolar addition of Et_3N produced three $Et_3NH^+[V^{VO}_2L^1]^-$ – $Et_3NH^+[V^{VO}_2L^3]^-$ complexes. Crystal and molecular structures of prepared complexes were determined by X-ray diffraction on single crystals.

In complex compounds vanadium is present in the anionic part of the compound, $[VO_2L]^-$, in a distorted square pyramidal environment. Anionic and cationic parts of all three complex compounds are connected *via* $N-H\cdots O$ and $C-H\cdots O$ hydrogen bonds. Anionic parts of the complex are mutually connected in crystal structure *via* $O-H\cdots O$, $C-H\cdots O$, $C-H\cdots N$ and $C-H\cdots S$ hydrogen bonds into endless chains (Fig. 1.)

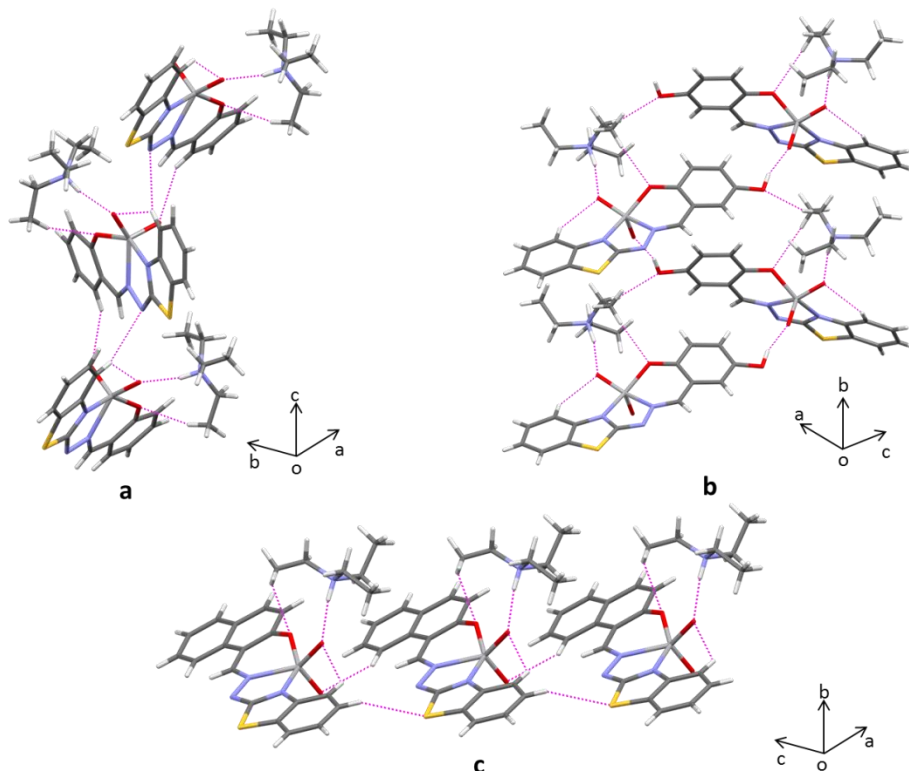


Fig. 1. Part of crystal packing of $Et_3NH^+[V^{VO}_2L^1]^-$ (a), $Et_3NH^+[VO_2L^2]^-$ (b) and $Et_3NH^+[V^{VO}_2L^3]^-$ (c)

The discovery of a natural occurring NASICON phase, $\text{NaMgAl}(\text{SO}_4)_3$

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Investigations of the Fumarolic environment at Eldfell, Surtsey and Hekla volcanos (Jakobsson et al. 2008) has led to the discovery of a number of new mineral species: eldfellite ($\text{NaFe}(\text{SO}_4)_2$) (Balic-Zunic et al. 2009), heklaite (KNaSiF_6) (Garavelli et al., 2010), jakobssonite (CaAlF_5) (Balic-Zunic et al. 2012), leonardsenite ($\text{MgAlF}_5(\text{H}_2\text{O})_2$) (Mitolo et al. 2013), oskarssonite (AlF_3) (Jacobsen et al. 2014). During this process, where Powder XRD assisted with SEM-EDS were used to characterise the different samples another new mineral was detected. From resemblances in the PXRD pattern it was supposed to be isostructural with NASICON-type $\text{NaMgF}(\text{SO}_4)$ (Slater and Greaves 1994) while the EDS-analysis suggested a $\text{NaMgAl}(\text{SO}_4)_3$ composition. During a field trip to Eldfell in 2008 new samples were brought back to monitor development of fumarolic minerals through time. Here, we discovered two types of the same mineral, with differing crystal lattice dimensions. The chemical analysis suggested presence of $\text{NaMgAl}(\text{SO}_4)_3$ with some substitution of K for Na. To clarify the case, we have attempted to synthesize under natural environment conditions (the Fumaroles had a temperature around 300°C measured in situ) a series of compositions between $\text{NaMgAl}(\text{SO}_4)_3$ and $\text{KMgAl}(\text{SO}_4)_3$. The syntheses were made from mixtures of stoichiometric proportions of Na_2SO_4 , MgSO_4 , Al_2SO_4 , which came in different hydrated forms, and K_2SO_4 .

We successfully synthesized the end members plus all intermediate members of the solid solution series, confirmed by PXRD analysis.

It seems that K has a vital kinetic influence in the formation of the crystals. The compound with a K-fraction close to the most commonly detected composition of natural samples had a quickest growth from an amorphous state into crystalline.

As the formation is happening at elevated temperature and since the new mineral has a NASICON-related structure, further crystallographic studies under high temperature are currently being conducted accompanied by thermal analysis.

Extending the chemistry of krypton

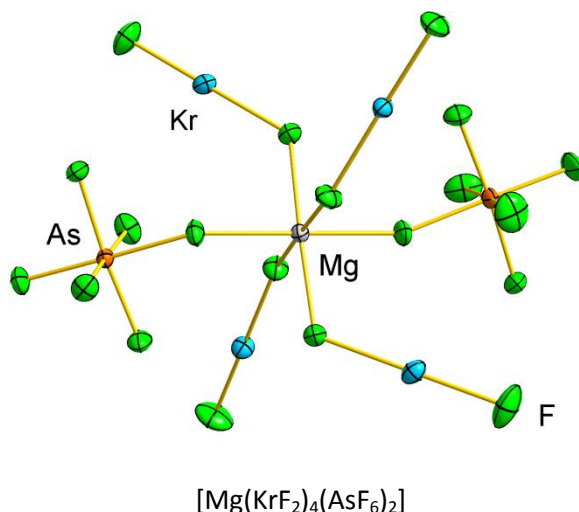
Matic Lozinšek, Hélène P. A. Mercier, and Gary J. Schrobilgen

Department of Chemistry, McMaster University, Hamilton, Ontario, Canada

Progress in the krypton chemistry has been severely hampered by the extreme oxidative fluorinating abilities of its compounds which are often coupled with their thermodynamic and kinetic instabilities. In order to successfully synthesize, isolate, handle, and structurally characterize krypton compounds, special experimental techniques need to be employed to surmount difficulties associated with their instabilities and reactivity. This involves the use of low-temperature Raman spectroscopy and low-temperature single-crystal X-ray diffraction. Only one krypton compound can be synthesised from the elements, albeit under cryogenic conditions, namely the thermodynamically unstable compound KrF_2 , which serves as the precursor for all other krypton compounds (Lehmann *et al.*, 2002; Lozinšek & Schrobilgen, 2016).

Owing to its fluoride ion donor properties, KrF₂ can function as a ligand forming fluoride-bridged adducts (Brock *et al.*, 2013). Its fluorobasicity has been exploited for the coordination of KrF₂ to the naked metal cation Mg²⁺, to give the Kr–F⋯Mg bridged adduct, [Mg(KrF₂)₄(AsF₆)₂] (see figure) and its solvate [Mg(KrF₂)₄(AsF₆)₂]·2BrF₅ – the first examples of KrF₂-ligated main-group metal complexes (Lozinšek *et al.*, 2017). Krypton difluoride was also shown to coordinate through one of its fluorine atoms to the non-metal center, Xe(VI), of the [XeF₅]⁺ cation, providing the first mixed noble-gas compounds, [XeF₅][AsF₆]·KrF₂ and [XeF₅][AsF₆]·2KrF₂. The aforementioned examples, employ the weakly coordinating anion, [AsF₆][–], which is essential for the coordination of weakly fluorobasic KrF₂ molecule.

Another area of krypton chemistry that has not been extensively explored is the formation of co-crystals. In this study, KrF_2 was also shown to co-crystallize with BrF_5 forming highly reactive low-melting solids in which KrF_2 interacts with Br(V) by forming weak $\text{Kr-F}\cdots\text{Br}$ bridges.



Brock, D. S., Schrobilgen, G. J. & Žemva, B. (2013). Noble-Gas Chemistry. In *Comprehensive Inorganic Chemistry*; Reedijk, J. & Poeppelemeier, K. Eds.; Elsevier, Oxford; **Vol. 1**, Chap. 1.25, pp. 755–822.

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Hydration and dehydration of saranchinaite

Evgeniya A. Lukina, Oleg I. Siidra, Evgenii V. Nazarchuk, Rimma S. Bubnova, Atali A. Agakhanov, Evgeniya Yu. Avdontseva, Vadim M. Kovrugin, Lidiya P. Vergasova, Stanislav K. Filatov, Gennady A. Karpov

Keywords: sulfates; hydration; dehydration

Minerals with sulfate anions are widely distributed in nature. There are more than 380 sulfate mineral species known to date. The most of known sulfate minerals are hydrated. A significant group of sulfate anhydrous minerals is formed as a result of high-temperature exhalative processes in fumaroles of different volcanoes

A new mineral saranchinaite, ideally $\text{Na}_2\text{Cu}(\text{SO}_4)_2$, was found in sublimates of Saranchinaitovaya fumarole, Naboko Scoria Cone, The Fissure Tolbachik Eruption (FTE) occurred in 2012–2013. Saranchinaite is extremely sensitive to moisture content in air and transforms to kröhnkite after one week exposure in open air at relative humidity of 87% and 25°C.

Discovery of saranchinaite allowed understanding decomposition of mineral kröhnkite and suggesting high-temperature behavior of many kröhnkite-type materials.

High-temperature X-ray diffraction studies were performed for kröhnkite from La Vendida mine and saranchinaite. Strongly anisotropic character of thermal expansion of kröhnkite remains very similar till its full decomposition. Full transformation of kröhnkite powder sample into saranchinaite is occurred at 200°C. Obtained saranchinaite reverses back into kröhnkite after exposure to open air. Thermal expansion in saranchinaite is significantly more complex than in kröhnkite. Saranchinaite demonstrates strongly anisotropic thermal expansion. Saranchinaite is stable till 475°C with the full decomposition after into tenorite, thénardite and unidentified phases.

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Uncovering phase boundaries in ternary piezoelectric ceramics

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Piezoelectrics are used in a wide variety of technology applications and currently their best performing compositions are lead-based. Legislative requirements will impose serious restrictions on the use of these lead-based materials in consumer devices over the coming years. Currently no viable lead-free alternative exists that operate over similar environmental ranges to existing lead-based materials.

It is well accepted that the electro-mechanical properties of piezoelectrics are maximised at Morphotropic Phase Boundaries (MPBs). Locating these phase boundaries can be difficult using traditional routes due to the vast numbers of samples required. A potential pathway for the discovery of otherwise unknown phase boundaries in higher order (ternary and quaternary) solid solutions is through combinatorial techniques. This involves the rapid synthesis and analysis of large numbers of compositions, through many combinations of a relatively small number of starting compounds.

A powder layering method was used to prepare binary combinatorial samples within the lead-free ternary system $\text{BT}_x\text{ST}_y\text{BNT}_{(1-x-y)}$ (where $\text{BT} = \text{BaTiO}_3$, $\text{ST} = \text{SrTiO}_3$, $\text{BNT} = \text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$). Scanning beam synchrotron x-ray diffraction was then used to analyse the structure as a function of composition to map out potential phase boundaries where the piezoelectric properties of the ceramics are expected to be a maximum.

A partial charge transfer between iodide ions and quinoid rings

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A series of cocrystals of tetrachloro- and tetrabromoquinone with organic iodide salts has been prepared and structurally characterised. Derivatives *N*-methylpyridinium were chosen as cations, due to their planarity and similar size to the quinones, while their electronic properties are radically different. While the iodide usually acts as an electron donor, reducing the quinone into the semiquinone radical [1,2], sometimes the co-crystals of the neutral quinone and the iodide appear. In the studied crystals, the common motive, or supramolecular synthon [3], has been identified: a sandwich-like I[−]...quinone...I[−] moiety with close contacts between the iodide anion and carbon skeleton of the quinoid ring (Fig. 1). Distances between the iodide and the ring centroid range between 3.6 and 3.85 Å, which is slightly shorter than sum of van der Waals radii for C and I. Interactions between π system aromatic ring and an anion are rarely observed, since aromatics are usually electron-rich; in the case of electron-depleted quinoid rings, anion... π contacts are more likely to form. In the studied cases, however, there is also a partial electron transfer between the iodide and the quinone which is noted by a change of colour: the neutral quinone is yellow, while the co-crystals and the semiquinone crystals are black.

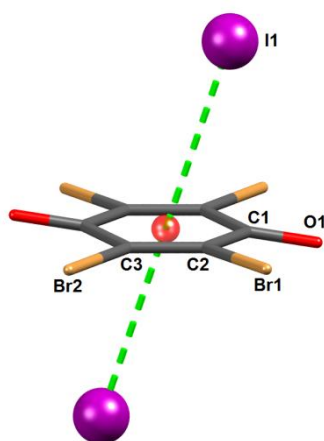


Figure 1. The I[−]...quinone...I[−] supramolecular synthon appearing in the studied structures.

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Four in ten millions: isomers of intrinsically vacant supramolecule

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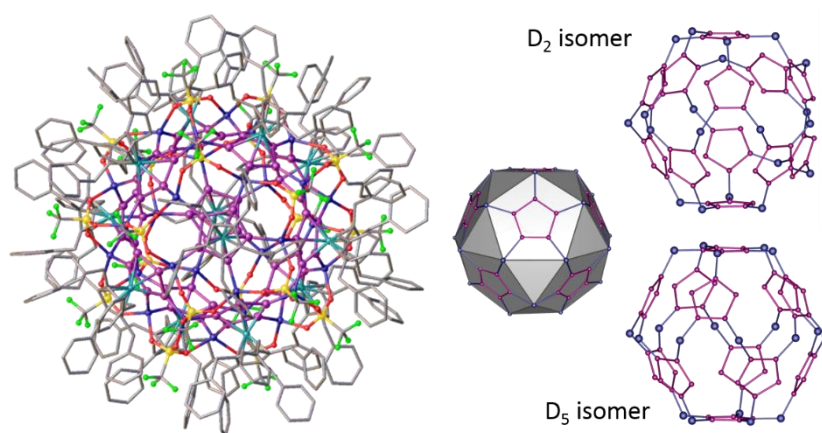
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Pentaphosphaferrocene, $[\text{Cp}^R\text{Fe}(\eta^5\text{-P}_5)]$ ($\text{Cp}^R = \eta^5\text{-C}_5\text{R}_5$, $\text{R} = \text{Me}$ (Cp^*), CH_2Ph (Cp^{Bn}), PhC_4H_9 (Cp^{BIG})), is known as a unique building block for construction of giant supramolecules [1]. Phosphorous atoms of *cyclo*- P_5 ligands are able to coordinate Cu^+ or Ag^+ (M^+) cations resulting in the formation of polynuclear complexes bearing inorganic spherical or elliptical $\text{M}_x(\text{P}_5)_y\text{X}_z$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$) core, which is surrounded by organic groups of R-substituted Cp ligands. Herein, we demonstrate the potential of $\text{Cu}(\text{CF}_3\text{SO}_3)$ for the construction of nano-sized supramolecule $[\{\text{Cp}^R\text{Fe}(\eta^5\text{-P}_5)\}_{12}\{\text{M}(\text{CF}_3\text{SO}_3)\}_{20-x}]$.

Triflate (CF_3SO_3^-) anions in this supramolecule play a role of spacers between M atoms. Every M atom in turn connects two P_5 rings. The resulting spherical inorganic core is intriguingly disordered. Thirty crystallographic positions of copper atom in the supramolecule form giant icosidodecahedron and therefore we can expect 30 metal cations, but there are only 20 triflate anions. Indeed, all M^+ positions are partly occupied and the sum of refined occupancy factors is close to 20 expected for neutral molecule. To understand the structure of individual supramolecule, we appealed to combinatorics. With the use of specially written program we systematically generated all



permutational isomers where 20 M^+ cations are distributed over 30 vertices of icosidodecahedron. In total 10,115,005 permutations were found. After we assumed that triflate anion must coordinate at least two M^+ cations, we found that there are not 10 million but only 4

isomers, 2 enantiomeric pairs with different point symmetry, namely, D_5 and D_2 .

DFT calculations for $\text{M} = \text{Cu}$ at the EDF1/SBKJC level proved that after geometry optimization the energy of the isomers differs by only 2.5 kcal/mol, which is well beyond the accuracy of the calculations for a system of this size. Therefore, all four isomers are equally possible and the crystallographic disorder of the M^+ cations can be interpreted as an average picture of the overlap of different isomers in different orientations.

This work was supported by ERC grant AdG339072-SELFPHOS.

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Topotactic formation of new high-pressure polymorph of L-alanine via methanol-water solvate

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Keywords: L-alanine, high-pressure, powder diffraction

Alanine, COO-CH(CH₃)-NH₃, is the second smallest amino acid after glycine. In contrast to the glycine, only one polymorph of L-alanine, the one stable under ambient conditions, has been unambiguously documented to date. The polymorphic solid-state transition at high pressure which has been reported in several publications (1, 2) could not be confirmed in later works.(3, 4) At the same time, the growth of spherulites of an unknown phase was observed, when a single crystal of L-alanine immersed in the ethanol-methanol-water (16:3:1) pressure-transmitting fluid in a diamond anvil cell was first compressed to 6 GPa, then decompressed to 5 GPa and kept at this pressure for weeks. (3) On decompression to 1.4 GPa this new phase starts to transform into another one, which eventually transformed into the ambient-pressure polymorph.

Here we report the existence of a new polymorph of L-alanine and of its solvate confirmed by a structure solution from X-ray diffraction, assisted by DFT calculations. The methanol-water solvate was obtained by compressing L-alanine in an ethanol-methanol-water mixture at pressure range 1.5–4.7 GPa. The new polymorph formed topotactically from this solvent on decompression below 1.4 GPa and remained stable until 0.4 GPa, after which it transformed back to the ambient pressure form.

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Opening pandora's box: chirality, polymorphism, and stoichiometric diversity in flurbiprofen/proline cocrystals

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Keywords: flurbiprofen, proline, cocrystals, liquid-assisted grinding, powder diffraction

Cocrystals are of interest to pharmaceutical industry as they allow varying pharmacological properties of drugs, e. g., improving bioavailability, dissolution rate, hygroscopicity, stability, etc., without changing the chemical nature of the active pharmaceutical ingredient (API). Moreover, owing to some specific properties, cocrystals can also be used in other crystallization applications, for instance, as a purification tool or for chiral resolution. Since a substantial part of drugs are chiral, the question how they respond to cocrystallization with chiral or nonchiral coformers is a hot topic for pharmaceutical industry.

This work focuses on studying profoundly flurbiprofen/proline system through cocrystallizing various combinations of enantiopure as well as racemic forms of the initial compounds. Flurbiprofen is a non-steroidal anti-inflammatory drug used to treat acute or chronic painful condition. Proline is an amino acid widely used as a conformer for various applications, e.g. for modifying the properties of APIs, chiral resolution, creation of amino acid derived semiconductor, etc.

In this contribution, we discuss an extreme complexity discovered for flurbiprofen/proline system: depending on the enantiopure or racemic forms used and cocrystallization conditions, the system exhibits polymorphism, up to 4 polymorphs for only one combination, is prone to forming cocrystal solvates and stoichiometrically diverse cocrystals (1 : 1, 2 : 1, 1 : 2, and even 1 : 3 flurbiprofen : proline). Analyzing the results of ball-milling, in-situ ball-milling, crystallization from solution, X-ray diffraction upon varying temperature, we established the conditions under which various cocrystal forms emerge; and exploring their structural peculiarities, we tried to understand better how chirality and zwitterionic nature of amino acids manifest themselves in cocrystallization.

Giant pentaphosphaferrocene-based supramolecules as molecular containers

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An inorganic analogue of ferrocene, pentaphosphaferrocene, $[\text{Cp}^{\text{R}}\text{Fe}(\eta^5\text{-P}_5)]$ ($\text{Cp}^{\text{R}} = \eta^5\text{-C}_5\text{R}_5$, $\text{R} = \text{Me}$ (Cp^*), CH_2Ph (Cp^{Bn}), PhC_4H_9 (Cp^{BIG})), is able to coordinate Cu^+ and Ag^+ cations resulting in either coordination polymers or in giant supramolecules [1-6]. The self-assembled supramolecules of 2.1 – 4.6 nm in diameter can be isolated in high yields using special crystallization technique. A tetrahedral coordination of Cu^+ together with the predetermined five-fold symmetry of the *cyclo*- P_5 ligand favors the formation of giant cages with fullerene or fullerene-like topologies.

Pentaphosphaferrocene-based supramolecules can play a role of molecular containers (Figure 1). Our early investigations proved that the Cp^* -based supramolecules can encapsulate $\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)$ as guest molecules [4]. Hereafter we found that the central cavities of the supramolecules can also include metallocene and cage molecules, fullerene C_{60} , and even molecules of metastable compounds such as white phosphorous and yellow arsenic [5]. Moreover, our recent results show that the ability of CuX ($\text{X}=\text{Br}, \text{I}$) to aggregation allows adapting supramolecule to encapsulate cationic guest molecules like Cp_2Co^+ .

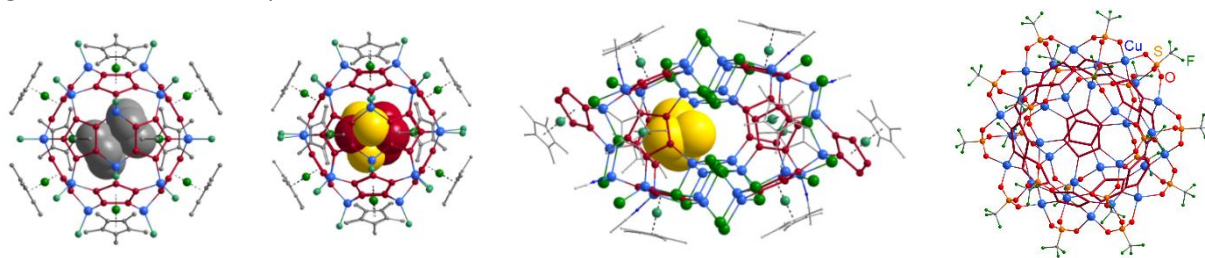


Figure 1. (left to right) Copper haide-based supramolecules encapsulating molecules of ferrocene, P_4S_3 , and As_4 . Inorganic core of a supramolecule based on copper triflate.

An alternative way to influence the structure of the supramolecule is to use salts of copper(I) and silver(I) with larger anions. First results show that single-layered quasi-spherical supramolecules with large central cavity can be obtained by using of RSO_3^- anions that can coordinate three metal atoms with donor oxygen atoms. The resulting inorganic $\text{M-anion-Cp}^{\text{R}}\text{Fe}(\eta^5\text{-P}_5)$ core resembles an icosidodecahedron, which is however essentially vacant in metal cation positions.

This work was supported by ERC grant AdG339072-SELFPHOS.

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Rational approach towards Ibrutinib solvates

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Solvates are easy to prepare and readily available multicomponent solids with still increasing potential of utility in drug products. Modern pharmaceutical research and production have to deal with ever reducing water solubility of the novel active substances. Dissolution is a crucial step for administration of the drug into human body and its influence on the bioavailability and overall utilization of the drug is straightforward. An interesting way how to overcome the dissolution problem is the utilization of multicomponent instead of monocomponent solid in the final product or as an intermediate step during production.

In our study, we have used a recently approved, water insoluble, oncological drug Ibrutinib as a model system. First, we selected several solvation candidates for Ibrutinib, based on the evaluation of the information about its known solid forms. The selected candidates were used to perform a slurry based and solution based solid state screenings. The resulting solids were characterized first by FT-Raman spectroscopy and possible hits were further analysed with XRPD. The success rate was evaluated for every screening set up with the best of 100 % success of preparing the solvate in the case of metastable polymorph slurry based screening. Overall success rate of our rational search for new solvates was 66 % (6 out of 9).

As a second part of the study, we have grown single crystals at every successful solvent. For all the single crystals we have solved the structure using X-ray diffraction data. The obtained structures were thoroughly evaluated with focus on the interactions and structural changes regarding the different partner molecules. Except the *para*-xylene system, the single crystal structures corresponded to the screening prepared powder samples. Two isostructural groups were identified between the prepared solvates, each containing two structures with the corresponding solvents. Even though, the solvent molecules were bound only by weak interactions in the solvates, a clear effect of the solvent molecular properties to the overall structure was observed.

In the third part, we have focused on the possible use of our new solvates in the real drug product. To determine the stability, we have measured the Raman spectra and XRPD for the stored samples after 3 months. Except for one solvate, the results were with no significant change. To evaluate the influence to the bioavailability, we have measured the dissolution profile for the selected solvates. We found that, in compare to non-solvated forms of the API, the formation of the solvate increased the dissolution rate up to 8.5 times.