Hrvatska Akademija Znanosti i Umjetnosti
Hrvatska Kristalografska Zajednica

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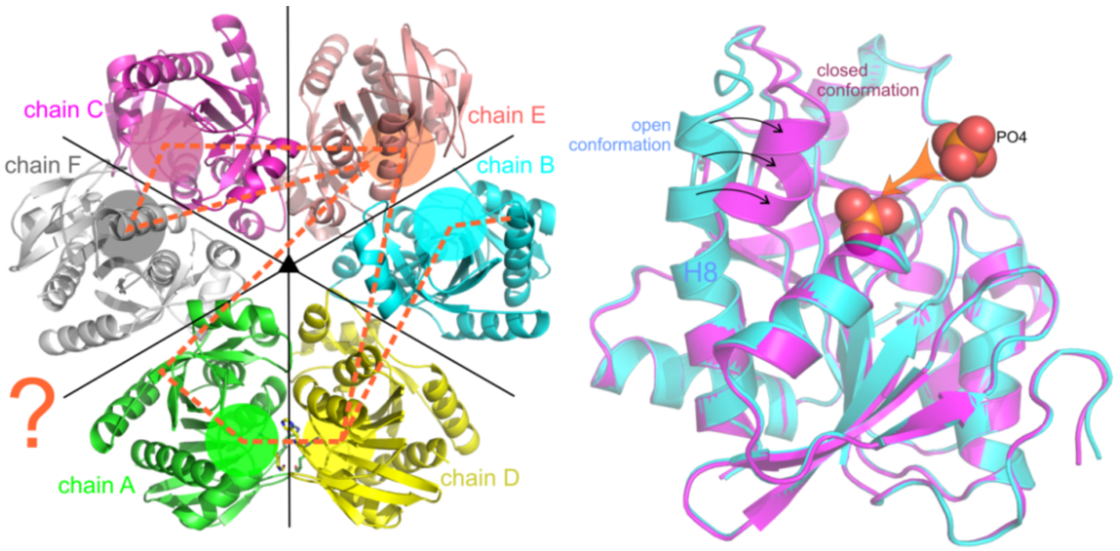
Croatian Academy of Sciences and Arts
Croatian Crystallographic Association

Faculty of Chemistry and Chemical Technology,
University of Ljubljana

The Twenty-Sixth Croatian-Slovenian Crystallographic Meeting

Poreč, Croatia, June 13 - 17, 2018

Book of Abstracts



The overall structure of hexameric nucleoside phosphorylases can be viewed as a trimer of dimers arranged in an approximate 32 point group symmetry (left). It is likely that active sites communicate between themselves through a yet unknown allosteric mechanism (indicated by orange dashed lines). Each monomer can be found in open and closed active site conformation. The active site is closed by segmentation of the terminal helix H8. The influence of binding of phosphate, one of the two substrates, on this conformational change is still not completely understood (right).

Zoran Štefanić, *Purine nucleoside phosphorylases: understanding enzyme mechanism and allosteric pathways*, plenary lecture, *The Twenty-Sixth Croatian-Slovenian Crystallographic Meeting*, Poreč, Croatia, June 13-17, 2018

PROGRAMME

CROATIAN CRYSTALLOGRAPHIC ASSOCIATION
FACULTY OF CHEMISTRY AND CHEMICAL TECHNOLOGY,
UNIVERSITY OF LJUBLJANA

The Twenty-Sixth Croatian-Slovenian Crystallographic Meeting – CSCM26

Poreč, Croatia, June 13 - 17, 2018

Programme book

The Twenty-Sixth Croatian-Slovenian Crystallographic Meeting will be held in the HOTEL VALAMAR DIAMANT, POREČ, CROATIA, from Wednesday to Sunday, June 13 - 17, 2018.
The opening of the Meeting will take place on Thursday at 9:00.

Honorary Chairs
Stanko Popović, Zagreb
Ivan Leban, Ljubljana

Chairs of the Meeting
Dubravka Matković-Čalogović, Zagreb
Anton Meden, Ljubljana

Chair *of the Scientific and Organizing Committee*
Željko Skoko, Zagreb

Scientific and Organizing Committee Members
Mario Cetina, Zagreb
Amalija Golobič, Ljubljana
Marijana Jurić, Zagreb
Teodoro Klaser, Zagreb
Matic Lozinšek, Ljubljana
Andrej Pevec, Ljubljana
Marta Počkaj, Ljubljana
Michele Zema, Pavia

The Meeting is organized jointly by the *Croatian Crystallographic Association* and the *Faculty of Chemistry and Chemical Technology, University of Ljubljana*

Wednesday, June 13, 2018

18^{00}-19^{00} Registration

19^{00} Welcome drink

Thursday, June 14, 2018

8^{30}-9^{00} Registration of participants

9^{00}-9^{10} Opening of the Meeting Ž. Skoko, D. Matković-Čalogović, A. Meden

SHORT ORAL CONTRIBUTIONS CHAIRS: K.Molčanov, I. Turel

9^{10}-9^{25} Anton Meden, Jernej Stare, Dušan Hadži
X-ray Powder Diffraction and Quantum Calculations Used to Determine the Structure of Pentadecafluorooctanoic Acid Hydrate

9^{25}-9^{45} Vladimir Stilinović, Dominik Cinčić
Coexistence of halogen and hydrogen bonds in crystal structures – competition, cooperation and antagonism

9^{45} -10^{00} Martin Adam, Holger Ott,Tobias Stuerzer, Michael Mrosek, Michael Ruf, Bruce C. Noll, Matthew Benning, Juergen Graf
Best Data Quality from D8 QUEST and D8 VENTURE

10^{00}-10^{20} Stanko Popović
Quantitative Phase Analysis by XRD – Simple Routes – New Perspectives / Applications

10^{20}-10^{30} Franc Požgan, Miha Drev, Uroš Grošelj, Franc Perdih, Jurij Svete, Bogdan Štefane
Atropisomerism in hexapyridylbenzenes

10^{30} -11^{00} Coffee break

PLENARY LECTURE CHAIR: M. Cetina

11^{00}-12^{00} **Andrzej Katrusiak**
High-pressure effects in hydrogen-bonded crystals

SHORT ORAL CONTRIBUTIONS CHAIRS: D. Matković-Čalogović, A. Meden

12^{00}-12^{15} Teodoro Klaser, Jasminka Popović, Panče Naumov, Michele Zema, José Fernandes, Željko Skoko
Is the thermosalient effect without phase transition possible?

12^{15}-12^{25} José A. Fernandes, Teodoro Klaser, Željko Skoko
Thermosalent Behavior on the Dehydration of Scopolamine Bromide Hydrate

12^{25}-12^{35} Krištof Kranjc and Franc Perdih
Preparation and Characterization of Cycloadducts with 3,9-Dioxatricyclo[5.2.2.0^{2,6}]undec-10-ene-4,8-dione Skeleton

12^{35}-12^{45} Tino Šeba, Vladimir Stilinović
Iodoform – a forgotten halogen bond donor

12^{45}-12^{55} Miha Drev, Uroš Grošelj, Franc Perdih, Jurij Svete, Bogdan Štefane, Franc Požgan
Molecular Structure of Heteroleptic Ruthenium(II) Complex Containing a Bidentate Bispyridyl-pyrimidyl Ligand

12^{55}-13^{10} Marcus J. Winter
Advances in X-ray crystallography

13^{10} -16^{00} Lunch break

SHORT ORAL CONTRIBUTIONS

CHAIRS K. KRANJC, Z. ŠTEFANIĆ

16^{00}-16^{15} Gligor Jovanovski, Pançe Naumov, Branko Kaitner, Durga Prasad Karothu, Ilma Jahović
Structural Evidence for Molecular Saccharin Embedded in Ionic Saccharinates of Rubidium and Cesium

16^{15}-16^{35} Albert Guskov
Transport of glutamate in archaea and eukaryotes

16^{35}-16^{50} Patrick Shaw Stewart
New strategies to improve productivity - rMMS microseeding for crystallization and DLS for cryoEM

16^{50}-17^{00} Ivana Kekez, Mario Kekez, Mario Stojanović, Jasmina Rokov-Plavec, Dubravka Matković-Čalogović
Revealing the structure of the first plant aminoacyl-tRNA synthetase at 2.3 Å

17^{00}-17^{30} Coffee break

PLENARY LECTURE

CHAIR: S. POPOVIĆ

17^{30}–18^{30} Paolo Scardi
SRXRD of metal nanocrystals: learning from mistakes

SHORT ORAL CONTRIBUTIONS

CHAIRS: A. TONEJC, F. POŽGAN

18^{30}-18^{40} Petra Stanić, Katarina Lisac, Vinko Nemec, Dominik Cinčić
Halogen-bonded cocrystals of an imine derived from N-aminomorpholine and 4-nitrobenzaldehyde: a playground for halogen bonding

18^{40}-19^{00} Krešimir Molčanov, Biserka Kojić-Prodić, Vladimir Stilinović, Zhongyu Mou, Miklos Kertesz, Bruno Landeros-Rivera, Jesús Hernández-Trujillo
Two-electron multicentric covalent bonding: how many centres?

19^{00}-19^{10} Luka Šmital, Mladen Borovina, Ivan Kodrin, Marijana Đaković
Computational study of hydrogen bond in systems of selected acetylacetonato complexes of Cu^{II} – theory vs. Experiment

19^{10}-19^{20} Wilfried Gille
Isotropic, linear particle growth and the parallel body set problem in SAS

19^{20}-19^{30} Nikola Jakupec, Vladimir Stilinović
Halogen Bonding in Halogenopyridinium Hexacyanoferrates

Friday, June 15, 2018

SHORT ORAL CONTRIBUTIONS

CHAIRS: B. MODEC, I. KEKEZ

8^{30}-8^{40} Marin Liović, Nikola Bedeković, Vladimir Stilinović, Dominik Cinčić
Cocrystalization of halogenide salts of organic bases with 1,4-diiodotetrafluorobenzene

8^{40}-8^{50} Mladen Borovina, Ivan Kodrin, Marijana Đaković
Can MEPs obtained from DFT calculations be used to a priori determine the effectiveness of the employed supramolecular strategies?

8^{50}-9^{05} Tomislav Piteša, Vladimir Stilinović, Ivan Ljubić, Vinko Nemec, Dominik Cinčić
Structural and DFT study of pyridine and imine nitrogen atoms as halogen bond acceptors: interplay of halogen bonds in the solid state

9^{05}-9^{15} Matjaž Kristl, Amalija Golobič, Nejc Babič, Brina Dojer
Synthesis and structure of a new iron(II) coordination compound with isonicotinamide

9^{15}-9^{30} Alen Bjelopetrović, Stipe Lukin, Ivan Halasz, Krunoslav Užarević, Ivica Đilović, Dajana Barišić, Ana Budimir, Marina Juribašić Kulcsár, Manda Ćurić

X-Ray Analysis of Intermediates and Products involved in Solid-State C–H Bond Activation by Pd(II) Chloride Precursors

9^{30}-9^{40} Very short break

KEYNOTE LECTURE   CHAIR: G. GIESTER

9^{40}-10^{40} **Lutz Nasdala**
Structural radiation damage in minerals: What can we learn?

10^{40}-11^{00} Coffee break

PLENARY LECTURE   CHAIR: Ž. SKOKO

11^{00}-12^{00} **Serena C. Tarantino**
Crystals' warm-up, stretching and ... workout!

SHORT ORAL CONTRIBUTIONS   CHAIRS M. JURIĆ, M. LOZINŠEK

12^{00}-12^{10} Božena Lovrić, Mladen Borovina, Marijana Đaković
Supramolecular synthesis of Co^{II} *and* Ni^{II} *complexes with acetylacetonate derivatives and pyridyl oximes*

12^{10}-12^{25} Barbara Modec, Petra Stare, Janez Košmrlj
A solved mystery? A novel zinc(II) ammine complex

12^{25}-12^{35} Aleksandar Meštrić, Ivana Pavličić, Sandra Čičić, Nenad Judaš
Combined mechanochemical and solution synthesis of copper(II) carboxylates

12^{35}-12^{45} Iztok Turel, Katja Traven, Branko Stanovnik, Julia Koziskova, Jozef Kožíšek
Organometallic ruthenium(II) complexes with selected N,N-donor ligands – interesting systems where also concomitant polymorphism was observed

12^{45}-12^{55} Andrej Pevec, Anja Sedminek, Janez Košmrlj
Thiosemicarbazides and Thiosemicarbazones as Ligands in Ni(II) Coordination Compounds

12^{55}-13^{05} Mario Cetina, Lucija Ptiček, Livio Racané
Intermolecular interactions in two cyclic amidino-derivatives built three-dimensional network

Afternoon - Excursion

Saturday, June 16, 2018

SHORT ORAL CONTRIBUTIONS   CHAIRS A. PEVEC, V. STILINOVIĆ

8^{30}-8^{40} N. Penić, M. Borovina, D. Pajić, M. Đaković
Supramolecular architectures of copper(II) halide complexes with amine and lactame derivatives of pyrazine and pyrimidine

8^{40}-8^{50} G. Dražić, G. Štefanić, T. Jurkin, M Gotić
Impact of cadmium and phosphate ions on the hematite nanorings formation

8^{50}-9^{00} Sara Cepić, Katarina Lisac, Dominik Cinčić
One-pot mechanochemical synthesis of a metal-based halogen bonded cocrystal with the $CoCl_2L_2$ *building block*

9^{00}-9^{10} Toni Grgurić, Nikola Bregović, Vladimir Stilinović
The study of pyridine adducts of $VO(acac)_2$ *in the solid state and solution*

9^{10}-9^{20} Darko Vušak, Dubravka Matković-Čalogović, Biserka Prugovečki

Supramolecular diversity in copper(II) complexes with L-homoserine/L-serine with heterocyclic bases

9^{20}-9^{30} Nikola Bedeković, Marta Klepić, Vladimir Stilinović, Dominik Cinčić
Influence of the intramolecular hydrogen bonding on structures and stability of adducts of copper and zinc b-diketonates with N-donor ligands

9^{30}-9^{40} Alen Bjelopetrović, Stipe Lukin, Ivan Halasz, Krunoslav Užarević, Ivica Đilović, Dajana Barišić, Ana Budimir, Marina Juribašić Kulcsár, Manda Ćurić
X-Ray Identification and Characterization of Azobenzene Palladacycles Obtained by Solid-State C–H Bond Activation

9^{40}-9^{50} Kristina Smokrović, Ivica Đilović, Dubravka Matković-Čalogović
Structural characterization of 3D coordination polymers of copper(II) and short, uncharged side chain amino-acids with a 4,4'-bipyridine linker

9^{50}-10^{05} Lidija Kanižaj, Krešimir Molčanov, Marijana Jurić
Chloride- and oxalate-bridged heterometallic $[\mathrm{Cu^{II}Cr^{III}}]$ *compounds with 2,2′:6′,2″-terpyridine – the influence of the starting copper(II) salt*

10^{05}-10^{15} Mateja Pisačić, Marijana Đaković
Understanding the role of weak interactions in responsivness of molecular crystals to external mechanical stimuli

10^{15}-10^{25} Robert Katava, Gordana Pavlović
Dioxovanadium(V) complexes with 2-benzothiazolyhidrazones as potential antitumor agents

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10^{25}-11^{00} Coffee break

PLENARY LECTURE

CHAIR: A. MEDEN

11^{00}–12^{00} **Nataša Zabukovec Logar**
Crystallography in Microporous Materials Research…

SHORT ORAL CONTRIBUTIONS

CHAIRS: A. M. TONEJC, E. GORESHNIK

12^{00}-12^{15} A. Stricker, J. Wiesmann, J. Graf, C. Michaelsen
Upgrading Home-Lab X-ray Diffractometers with Incoatec´s Unique Microfocus Source

12^{15}-12^{30} Bogdan Kotur, Volodymyr Levytskyy, Volodymyr Babizhetskyy
Crystal chemistry of metal-rich R–T–C carbides

12^{30}-12^{45} Evgeny Goreshnik, Lev Akselrud, Zoran Mazej
Incommensurately modulated crystal structures of $[\mathrm{XeF_5}][\mathrm{As_xSb_{1-x}F_6}]$ *(x ~0.3 and ~0.5)*

12^{45}-13^{00} Matic Lozinšek, Katarina Starkl Renar, Jernej Iskra
Structural Investigations of Organic Geminal Dihydroperoxides

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13^{10}-16^{00} Lunch break

SHORT ORAL CONTRIBUTIONS

CHAIRS: M. KRISTL, J.POPOVIĆ

16^{00}-16^{10} Marijana Jurić, Lidija Kanižaj, Jasminka Popović, Lidija Androš Dubraja
Preparation of the $\mathrm{Ba_2CrNbO_6}$ *and* $\mathrm{NiNb_2O_6}$ *Oxides by Thermal Decomposition of the Mixture of Oxalate Precursors*

16^{10}-16^{20} M. M. Radanović, Lj. S. Vojinović-Ješić, M. V. Rodić. V. M. Leovac
Crystallographic study of cadmium(II) complexes with 2-acetylpyridine-aminoguanidine and bromide as coligand

16^{20}-16^{30} Nikola Tasić, Jovana Ćirković, Aleksandra Dapčević, Lidija Ćurković, Vesna Ribić, Milan Žunić, Goran Branković, Zorica Branković
$\mathrm{Ag/TiO_2}$ *nanoparticle composites and their photocatalytic performance*

16^{30}-16^{40} Andreas Ertl, Gerald Giester, Ekkehart Tillmanns

Tetrahedrally-coordinated boron in Fe-bearing dravite from a metamorphic schist from Brandrücken, Weinebene, Koralpe, Styria, Austria

16^{40}-16^{50} Tamara Đorđević, Ljiljana Karanović, Zvonko Jagličić
A new copper(II) arsenate, $Na_2Cu_3(AsO_3OH)_4{\cdot}4H_2O$ containing discrete $[Cu_3O_{12}]^{18-}$ units: synthesis, crystal structure and magnetic properties

16^{50}-17^{00} Jovana Ćirković, Danijela Luković Golić, Aleksandar Radojković, Aleksandra Dapčević, Nikola Tasić, Mirta Čizmić, Goran Branković, Zorica Branković
$BiFeO_3$-based nanoparticles obtained by different synthetic routes and their structural, optical and photocatalytic properties

17^{00}-17^{30} Coffee break

PLENARY LECTURE **CHAIR:** J. POPOVIĆ

17^{30}–18^{30} **Zoran Štefanić, Marija Luić**
Purine nucleoside phosphorylases: understanding enzyme mechanism and allosteric pathways

SHORT ORAL CONTRIBUTIONS **CHAIRS** Ž. SKOKO, G. ŠTEFANIĆ

18^{30}-18^{40} Valentina Martinez, Nikola Bedeković, Vladimir Stilinović, Dominik Cinčić
Halogen-bonded complexes of perhalogenated hydrocarbons and benzoyl-4-pyridoylmethane

18^{40}-18^{50} Karla Kelemen, Krunoslav Užarević, Ivica Đilović
Proof-of-concept: flexible receptor in complexes with malonic acid

18^{50}-19^{00} Silvia-Maria Franov, Vinko Nemec, Dominik Cinčić
Cooperativity of halogen bonds in cocrystals of 4-halogenoanilines and 1,4-diiodotetrafluorobenzene

19^{00}-19^{10} Sara Marijan, Vinko Nemec, Vladimir Stilinović, Dominik Cinčić
Halogen bonded cocrystals of N-bromophthalimide with 2-chloro- and 2-bromopyridine

19^{10}-19^{25} Alen Bjelopetrović, Stipe Lukin, Ivan Halasz, Krunoslav Užarević, Ivica Đilović, Dajana Barišić, Ana Budimir, Marina Juribašić Kulcsár, Manda Ćurić
X-Ray Analysis of Intermediates and Products involved in Solid-State C–H Bond Activation by Pd(II) Chloride Precursors

19^{25}-19^{35} Babu A. Manjasetty
Indo-Italian Macromolecular Crystallography (MX) Beamline XRD2 at Elettra Synchrotron Light Source

19^{35}-19^{45} Award ceremony for:
(1) *IUCr award for best short oral presentation for young scientists*
(2) *Bruker award for best short oral presentation for young scientists*
(3) *Bruker award for best short oral presentation*

19^{45}-19^{50} Closing remarks A. MEDEN, D. MATKOVIĆ-ČALOGOVIĆ

20^{00} Meeting dinner

The Twenty-Sixth Croatian-Slovenian Crystallographic Meeting - CSCM26

is financially supported by

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The Twenty-Sixth Croatian-Slovenian Crystallographic Meeting - CSCM26

Poreč, Croatia, June 13 - 17, 2018

is held under the auspices of the

Department of Mathematical, Physical and Chemical Sciences

Croatian Academy of Sciences and Arts

PLENARY LECTURES

High-pressure effects in hydrogen-bonded crystals

Andrzej Katrusiak
Wydział Chemii , Uniwersytet im. Adama Mickiewicza, Poznań, Poland

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Pressure can efficiently modify the crystal structure, interactions of molecules, their conformations, and even pressure-induced topochemical reactions. Weak intermolecular interactions in molecular crystals and soft conformational parameters are usually most affected. This leads to considerable structural effects, such as monotonic compression, phase transitions, recrystallizations, changing compositions (*e.g*. preferential solvation/desolvation), new compounds, polymers *etc*.

Pressure-induced transformations at the microscopic level in crystal structures usually can be associated with the types of intermolecular interactions. This is particularly evident in the crystals with clearly distinguishable frameworks, such as coordination polymers (CPs) and metal-organic frameworks (MOFs), as well as in hydrogen-bonded and halogen-bonded compounds. In some cases, pressure can change the preferred types of interactions, which usually results in discontinuous transformations.

The advent of diamond-anvil cell (DAC) provides new opportunities for applying pressure in structural diffractometric studies. Relatively cheap and much more affordable compared to low-temperature attachments, the DAC has now become a standard equipment in many X-ray diffraction labs. Various sorts of scientific projects traditionally investigated only as a function of temperature and composition, owing to the DAC have now gained a new perspective of the pressure-induced changes.

The progress fueled by pressure studies in the structural transformations of hydrogen bonds and hydrogen-bonded crystals will be presented. Apart from the transformations of strong hydrogen bonds =OH···O- (e.g. see Ref. [1]), also the systematic effects of much weaker H-bonds (e.g. CH···N/O, NH···I) on the crystal compression [2,3] and possible amorphization [4] will be discussed for selected compounds.

This study was supported by the Polish National Science Centre, grant OPUS 10 2015/19/B/ST5/00262.

References

[1] A. Katrusiak, Structural origin of tricritical point in KDP-type *Ferroelectrics* **188** (1996) 5-10.
[2] S. Sobczak, A. Katrusiak*,* Zone-collapse amorphization mimicking the negative compressibility of a porous compound*, Cryst. Growth Des.* **18** (2018) 1082-1089*.*
[3] J. Marciniak, A. Katrusiak*,* Direct and Inverse Relations between Temperature and Pressure Effects in Crystals: A Case Study on o-Xylene, *J. Phys. Chem. C* **121** (2017) 22303-22309.
[4] M. Szafrański, A. Katrusiak, Photovoltaic hybrid perovskites under pressure, *J. Phys. Chem. Lett*. **8** (2017), 2496-2506.

SRXRD of metal nanocrystals: learning from mistakes

Paolo Scardi,[1]
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Research on metal catalysts has been revived by the advent of nanotechnology in the last twenty years. A growing literature shows a variety of methods to produce nanocrystals of specific shape and size, to enhance the selectivity of the catalytic response in the different chemical environments. At the same time characterization techniques have greatly evolved, especially concerning Transmission Electron Microscopy and several X-ray spectroscopies, supported by the unique properties of Synchrotron Radiation (SR).

X-ray diffraction (XRD) has been one of the first analytical techniques to benefit of SR. Much used in structural studies, SR XRD has a large and still mostly unexplored potential in microstructural analysis, especially when applied to powders made of identical (or nearly so) nanocrystals. As shown recently [1], SR XRD of Pd nanocubes shows interference fringes similar to those observed by coherent diffraction imaging on (much bigger) single crystals, thus allowing to obtain detailed information on the shape and average size of a statistically significant set of nanocrystals, including the effect of both static and dynamic atomic disorder.

The environmental conditions that can be produced during SR XRD measurements require proper consideration, for the interaction of the high-energy intense radiation with the atmosphere and catalytic surfaces. But problems and even mistakes can disclose a wealth of opportunities for in situ and in operando studies: oxidation and hydriding of metallic nanocrystals can be observed in a new light.

References

[1] P. Scardi, A. Leonardi, L. Gelisio, M.R. Suchomel, B.T. Sneed, M.K. Sheehan & C.-K. Tsung, Phys.Rev. B 91 (2015) 155414.

Crystals' warm-up, stretching and ... workout!

Serena C. Tarantino
Department of Earth and Environmental Sciences, University of Pavia, Italy

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With changing temperature *(warm up)*, crystals will expand (*stretching*) and sometimes undergo transformations of their structural or physical properties, as it is the case of jumping, bending or twisting crystals (*workout*). In this talk, examples will be shown of both inorganic and organic crystals, which exhibit the thermosalient effect, despite showing different structural behaviours with temperature causing them to jump.

Examples will include the jumping effect associated with the first-order tetragonal-to-cubic phase transition in $Mg_xCu_{1-x}Cr_2O_4$ spinel solid solution. In this structure, the cooperative Jahn-Teller distortion imposing the tetragonal symmetry can be suppressed either by increasing the temperature or by gradually substituting the d^9 Cu(II) cation with the spherical and closed-shell Mg(II) cation. It will be shown how the temperature variations of spinel crystal structures can be analysed by mode decomposition techniques and the structural evolutions inferred from the temperature dependences of the spontaneous strain and the associated order parameter [1]. Other examples will come from organic crystals (collaboration with Ž. Skoko, G. Ventruti and J. Popović) and include oxitropium bromide (OTB) and hydrated scopolamine methyl bromide (SMBH), where the jumping effects seems to be associated, respectively, with an isosymmetrical phase transition or with a dehydration/re-hydration process. Both transformations are responsible for a fairly large first-order jump, are reversible and show some hysteresis on cooling.

In all cases, we have used a newly developed HT device and crystal mounting methods to collect variable temperature single crystal X-ray diffraction (VT SC-XRD) data in situ. Our system is flexible and fully versatile for studies under different heating (up to ca. 1100°C) and atmospheric conditions, with no limitations to the rotation of goniometer circles. Crystal mounting in quartz vials (in air; in closed atmosphere of virtually any conditions; under vacuum) by making use of quartz wool to avoid mechanical stress on crystal surfaces is compatible with this set-up and proved particularly efficient in the study of jumping crystals, as quartz fibres are flexible enough to accommodate crystal movements at the transition.

References

[1] S.C. Tarantino, M. Giannini, M.A. Carpenter, M. Zema, Cooperative Jahn-Teller effect and the role of strain in the tetragonal-to-cubic phase transition in $Mg_xCu_{1-x}Cr_2O_4$, *IUCrJ*, **3**, 354-366, 2016.

Crystallography in Microporous Materials Research…

Nataša Zabukovec Logar[1]
[1] *National Institute of Chemistry, Hajdrihova 19, Ljubljana 1000, Slovenia*
University of Nova Gorica, Vipavska 13, Nova Gorica 5000, Slovenia

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Microporous solids, exemplified by aluminosilicates zeolites, are an important class of materials with pore sizes up to 2 nm, which have many applications as shape selective solid acid catalysts in the oil industry, for the production of fine chemicals and for separations using their molecular sieving capabilities. Understanding of their performance in the selected processes and the design of new materials first requires full insight into their atomic structure. This includes the determination of the three-dimensional open-framework structure and the nature of low-content active sites. The latter are most commonly associated with the framework metal atoms such as aluminium or transition-metals, which confer catalytic activity. The far more challenging but crucial issue when elucidating structure-property relationships is to monitor the processes in the bulk and at the surface of the materials at working conditions. Many times this requires elevated temperatures and pressures and very demanding design and operation of in-situ reaction cells.

Traditionally, the long-range order in crystalline zeolite structures has been studied by single-crystal X-ray diffraction. The pre-eminence of single-crystal structure analysis has been challenging for zeolite crystals due to their generally small volume. This has been a driving force for the development and constant improvement of powder diffraction methods in microporous materials research. In the recent years, structural chemistry of zeolites and related materials has been governed by a multi-technique characterisation approach. The advances in the use of single-crystal or powder X-ray, neutron and electron diffraction, as a backbone of structural characterisation, were achieved by the support of electron microscopy, diffuse scattering interpreted with pair-distribution functions and molecular modelling/simulations, anomalous scattering, etc. The new methods enabled structure determination of many exciting commensurately modulated zeolitic structures, as well as better understanding of correlated or non-correlated disorder as a key to materials functionality, including catalytic activity. Further developments are expected with the continuously improving landscape of synchrotron sources with hard X-rays, new theoretical approaches, as well as improvements in computers performance and instrumentation for data collection and processing. This will promote studies on smaller/thinner samples and in-situ time-resolved studies of crystallisation, catalytic and other processes on the sub-nano second time-scale. In the presentation, the power of the state-of-the art diffraction methods and multi-technique approach will be highlighted on recent examples from zeolite, aluminophosphate and metal-organic framework structural studies. Most relevant complementary spectroscopic and microscopic studies will be mentioned when appropriate.

Purine nucleoside phosphorylases: understanding enzyme mechanism and allosteric pathways

Zoran Štefanić,[1] Marija Luić,[1]
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Purine nucleoside phosphorylases (PNPs) have been the subject of our scientific interest for a number of years [1]. Despite much progress that has been made in understanding the catalytic mechanism of PNPs, there are still many pieces of the puzzle to be discovered. Recently, we have determined the first crystal structure of PNP from *Helicobacter pylori* (HpPNP) which is an essential enzyme of its purine salvage pathway [2]. HpPNP seems to possess some unusual features that distinguish it from other PNPs. Moreover, its crucial role in the purine salvage pathway of this serious human pathogen, makes it a very promising drug target [3]. As more and more crystal structures of this enzyme become available, the evidence grows of intricate communication, maybe even allosterically regulated, between the active sites [4]. Perhaps related to this, the distribution and variations in conformation of open and closed active sites in crystal structures is also growing, and HpPNP is displaying even some previously unobserved features [4]. Various approaches to tackle these open questions, that have crystal structures as a starting point, will be discussed.

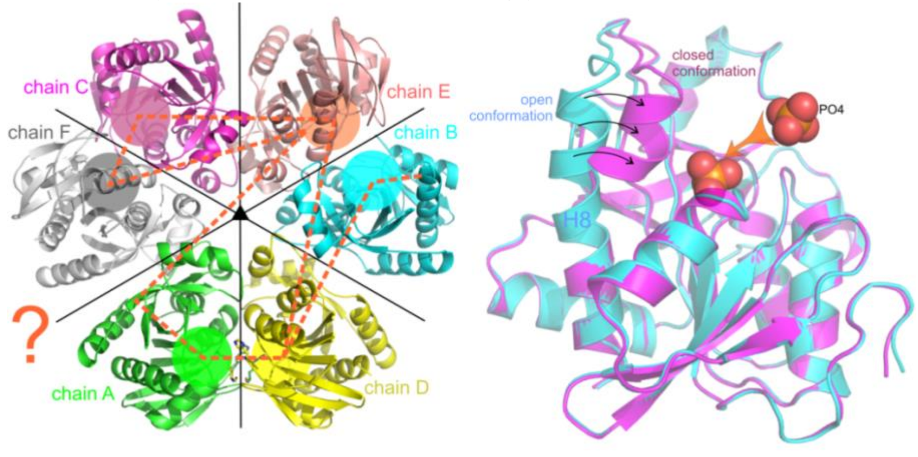

Figure 1: The overall structure of hexameric PNPs can be viewed as a trimer of dimers arranged in an approximate 32 point group symmetry (left). It is likely that active sites communicate between themselves through a yet unknown allosteric mechanism (indicated by orange dashed lines). Each monomer can be found in open and closed active site conformation. The active site is closed by segmentation of the terminal helix H8. The influence of binding of phosphate, one of the two substrates, on this conformational change is still not completely understood (right).

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KEYNOTE LECTURE

Structural radiation damage in minerals: What can we learn?

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The impact of corpuscular radiation, in minerals mainly due to alpha decays of the actinide elements U and Th, and their instable daughter nuclei, may lead to dramatic changes of physical properties of minerals and a general decrease in their chemical resistance. For instance, results of U–Th–Pb analyses obtained from radiation-damaged accessory minerals are often biased due to secondary loss of radiogenic Pb and other post-growth alteration. For sound interpretation of dating results, the underlying processes need to be understood by geochronologists. Another motivation of studying radiation-damaged minerals is the need to find suitable host forms for the long-term immobilization of nuclear waste.

This keynote lecture focuses at spectroscopic studies of naturally radiation-damaged and ion-irradiated minerals and other solids. The lecture starts with an introduction to processes of radiation-damage accumulation in natural minerals. Five research examples are presented in detail: (i) Effects of radiation damage on the electron back-scattering, studied by Raman and photoluminescence hyperspectral imaging. (ii) Effects of electron irradiation on radiation damage in zircon. (iii) Characterisation of ekanite, $Ca_2Th_{0.9}U_{0.1}Si_8O_{20}$, a radioactive gemstone from Sri Lanka. (iv) Heavy-ion irradiation of µm-thin lamellae of minerals, prepared using the focused-ion-beam technique. (v) Radiocolouration (near-surface "irradiation stains") of natural diamond.

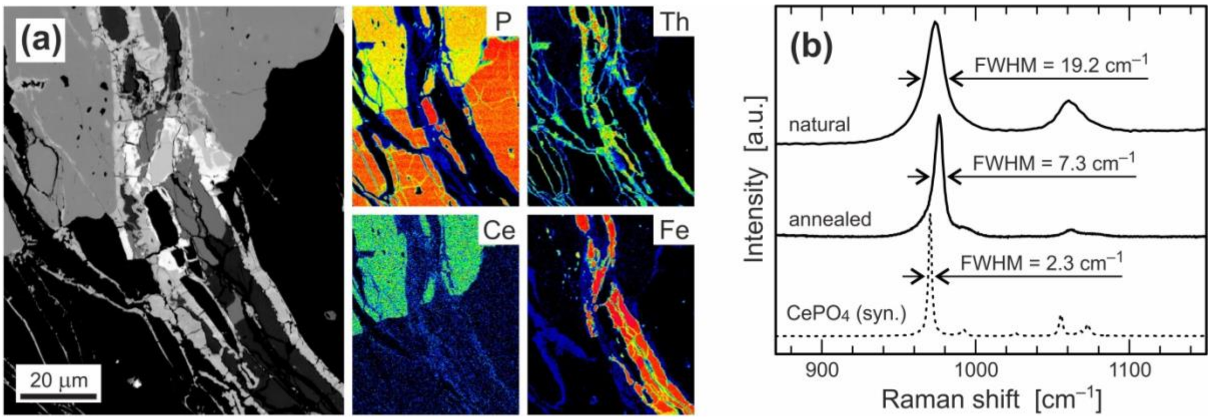

Figure 1: Radiation damaged and altered monazite–(Ce) from a pegmatite (Dillingøya island, Østfold district, Norway; cf. [1]). (a) BSE image of fractured monazite–(Ce) (gray) associated with apatite (black), along with four EPMA element distribution maps. After element mobilization, secondary Fe and Th phases were deposited in young fractures. (b) Raman spectra of the monazite–(Ce) before and after thermal annealing, along with a synthetic reference [2]. Note that the broadening of the main, symmetric PO_4 stretching band near 972 cm^{-1} is predominantly due to radiation damage, whereas the "chemical band broadening" is rather moderate.

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SHORT ORAL CONTRIBUTIONS

X-ray Powder Diffraction and Quantum Calculations Used to Determine the Structure of Pentadecafluorooctanoic Acid Hydrate

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The title compound ($C_7H_{15}COOH{\cdot}H_2O$) attracted attention due to a very short hydrogen bond ($R_{O\cdots O}$ ~ 2.5 Å) observed by vibrational spectroscopy. As its crystal structure was not known, several crystallization trials were performed, but only a rather poorly crystallized powder was obtained. The X-ray powder diffraction pattern (Cu$K_{\alpha 1}$ radiation, λ = 1.5406 Å) was only useful up to 53 °2θ, where peaks could still be seen above the background.

Indexing and the profile fit with the most probable space group $P2_1/c$ gave quite reliable unit cell with parameters of a=22.826(5), b=5.5204(3), c=11.115(4) Å, β =91.47(4) °. Structure solution trials resulted in a model that showed reasonable packing, but finer details were not accessible due to very low resolution of the diffraction data. Therefore, this coarse structure was optimized by periodic DFT calculations. Small variations of the initial model resulted in five DFT optimized structures, which were then tested against the experimental powder pattern. The correct structure was clearly recognized by the best match between the calculated and experimental powder patterns.

The structure (Fig. 1) reveals expected double layer packing and fine details of the hydrogen bonding pattern, which is similar to that in the oxalic acid dihydrate and will be presented along with some other details.

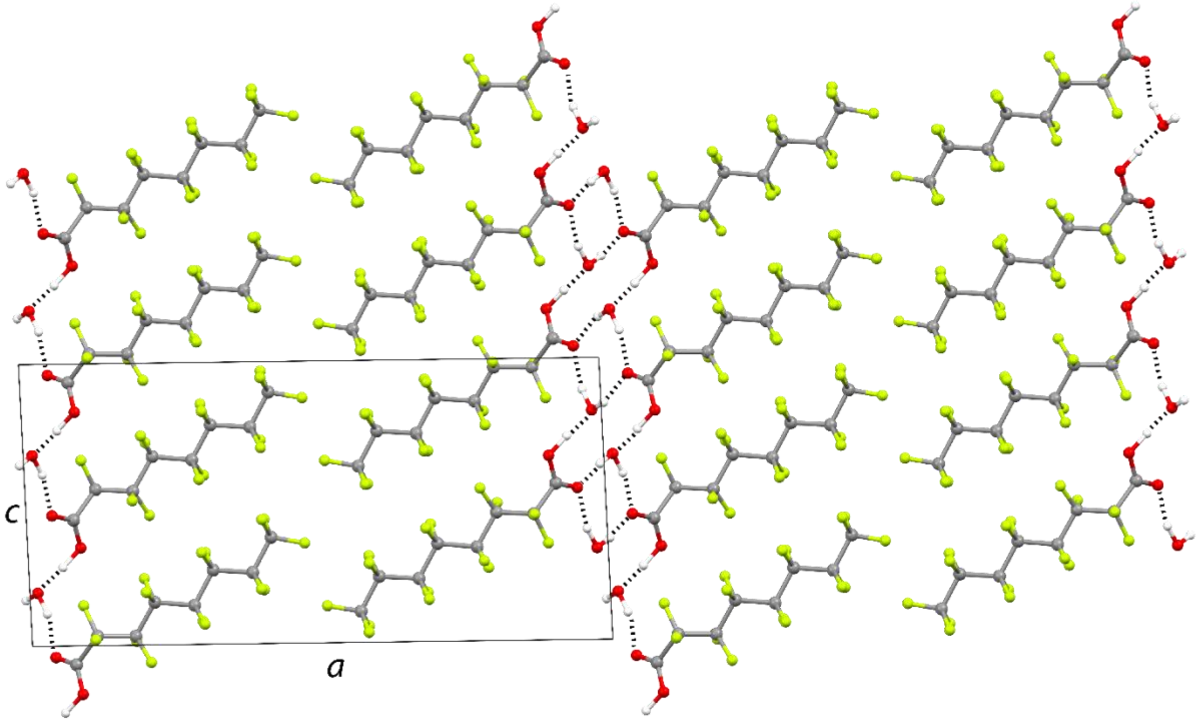

Figure 1: Structure of PDFO·H_2O viewed along the b axis and with labeled unit cell and H-bonds.

Coexistence of halogen and hydrogen bonds in crystal structures – competition, cooperation and antagonism

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Over the past couple of decades, the importance of halogen bonds in crystal engineering is constantly increasing. This is predominantly due to their strength and directionality which are commonly claimed to be close to those of hydrogen bonds – the generally accepted benchmark for evaluation of intermolecular interactions in supramolecular chemistry and crystal engineering. In this contribution, the comparison of halogen and hydrogen bonding will be made by studying structures in which halogen and hydrogen bonds coexist. In this manner some of similarities and differences between the two interactions will be discussed.

In the first part of the talk we shall concentrate on the competition between halogen bond and 'classical' strong hydrogen bonds (N–H···O and N–H···N). As a model system for this study we have employed cocrystals of *N*-halogenoimides with aminopyridines. *N*-Halogenoimides (*N*-iodoimides in particularly) have been shown to be extremely strong halogen donors, with halogen bond energies larger than those of equivalent hydrogen bonds.[1] In cocrystals of *N*-iodoimides with aminopyridines, the imide and pyridine nitrogen always binds through a very short N–I···N halogen bond, while the amino group participates in N–H···O – hydrogen bonds with imine oxygen atoms, in much the same way as aromatic groups form C–H···O interactions in equivalent structures without strong hydrogen donors.[2] The dominant interaction in all structures is clearly the halogen bond.

In the second part we shall observe the interdependence of halogen and hydrogen bonds in salts and cocrystals of organic acids of various strengths with *meta*-halogenopyridines, a series of rather modest halogen bond donors. The dominant interaction in these structures is O–H···N (or $O^-\cdots H–N^+$) hydrogen bond between the acid and the pyridine. This bond however can be affected by the additional halogen bond. The effect can be measured within series of isostructural compounds derived from halogenopyridines, as the steric properties and pK_a values change very little with the change of the halogen, the only significant variable being the ability of the halogenopyridine to form halogen bond (which increases with the size of the halogen). In this way we were able to study the subtle interplay of halogen and hydrogen bond, revealing instances of both cooperativie and antagonistic interdependence between the two interactions.

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Best Data Quality from D8 QUEST and D8 VENTURE

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Modern chemical and biological crystallography continuously pushes the limits to ever smaller samples with typically weaker diffraction properties. Here we will present new software and hardware components which tremendously improve the performance of laboratory instrumentation: the new IµS DIAMOND source the new PHOTON III X-ray detector and the new IDEAL refinement routine.

- The air-cooled IµS DIAMOND microfocus sealed tube source uses a unique diamond hybrid anode technology to produce intensities similar to modern microfocus rotating anodes. The anode consists of a diamond substrate coated with copper. The high thermal conductivity, low thermal expansion and extreme hardness of diamond make it an ideal substrate, which allow for higher power loading and greater long-term stability of the source, delivering the brightest micro-focus sealed tube ever. As of today another problem associated with high-end X-ray sources is gone: high maintenance costs. The IµS DIAMOND does not require any routine maintenance and has the same legendary life time which makes the IµS system the most popular microfocus X-ray source for more than a decade.
- The PHOTON III is a new CPAD (charge-integrating pixel array detector), which utilizes a mixed-mode approach for data collection. The weak reflections are measured in photon-counting mode and the strong reflections are measured in integrating mode. Consequently, the ultra-sensitive PHOTON III detector can collect very weak reflections without suffering from charge-sharing or non-linearity effects common to other photon-counting detectors.
- The introduction of shutterless-mode operated, large active-area detectors has dramatically improved the accessibility of data to 0.5 Å and beyond. Today, these data are available in only one detector setting with short exposure time in excellent quality. Traditional structure refinement uses an Independent Atom Model (IAM), which beyond the establish 0.83 Å reveals electron density, which cannot be modelled appropriately. Our new IDEAL program expands the model taking bond-electron and lone pair density contributions additionally into account. The density information is derived from the INVARIOM database of ab initio calculations of model compounds. IDEAL is fully integrated into the APEX3 software suite.

Bruker's D8 QUEST and D8 VENTURE both take advantage of all improvements in source, detector and software technology, leading to a previously unknown level of performance.

Quantitative Phase Analysis by XRD – Simple Routes – New Perspectives / Applications

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The elemental composition of a multiphase material can be determined by chemical and spectroscopic techniques. However, these techniques face a difficulty in distinguishing the chemical identity of crystalline phases present in the material and in derivation of the fractions of particular phases. X-ray powder diffraction has been proved to be an ideal technique for the analysis of a multiphase material. The intensities of diffraction lines of a given phase are proportional to its fraction and a quantitative analysis can be performed after the application of the correction for the absorption of X-rays in the material. [1, 2]

Simple routes of quantitative X-ray diffraction phase analysis of a multiphase material are presented with a special attention paid to the doping methods: (*i*) simultaneous determination of the fractions of several phases using a single doping [3-5]; (*ii*) determination of the fraction of the dominant phase [4,5]. The applicability of the doping methods is stated and the optimum conditions to minimize systematic errors are discussed [6-8]. The problem of overlapping of diffraction lines can be overcome by combining the doping method (*i*) and the individual profile fitting method, thus performing the quantitative phase analysis without the reference to structural models of particular phases [9]. Recent approaches in quantitative phase analysis are mentioned in short, as well as new perspectives/applications, *e.g.* in study of decomposition of supersaturated solid solutions, namely intermetallic alloys [10,11]. The fraction of a precipitate formed during ageing of the supersaturated solid solution [β(Zn) in case of Al-Zn alloys] at high temperature can be estimated through these steps: quenching the alloy to RT in order to stop or essentially to slow down the decomposition process; doping the quenched alloy by a substance having the same chemical composition and crystal structure as the precipitate (Zn in case of Al-Zn alloys); taking into account a possible (although slow) continuation of the decomposition process at RT.

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Atropisomerism in hexapyridylbenzenes

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Hexaarylbenzenes have attracted considerable interest due to their potential application in organic light-emitting diodes, molecular receptors and chemosensors, redox materials, photochemical switches, and liquid crystalline materials [1]. Their synthesis has been in general realized either by high temperature Diels-Alder reaction between diarylacetylenes and perarylated cyclopentadienones [2], or by metal-based catalytic [2+2+2] cyclotrimerization of corresponding 1,2-disubstituted acetylenes [3].

We have developed a simple approach to the synthesis of hexapyridylbenzenes relying on multiple C–H bond activation of heteroarylbenzenes. The reactions proceeded selectively in the presence of ruthenium(II) catalyst system, which assured three C–H bond functionalizations of 1,3,5-tris(2-pyridyl)benzene (**1**) with 2-bromo-6-methylpyridine in water under microwave heating (Figure 1). The radial chromatography allowed the separation of two isomers of C_3 symmetric star-shaped product **2** due to restricted rotation of pyridyl units at room temperature. The X-ray analysis revealed that the two isomers differ only in rotation of one methyl-containing pyridyl group. The energy barrier for interconversion of these two rotamers is high enough to separate the two thermodynamically stable atropisomers as concluded from DFT calculations.

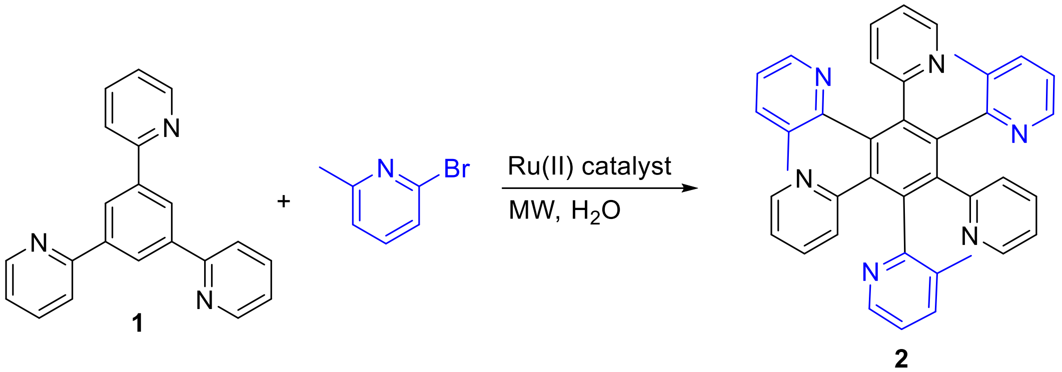

Figure 1: Synthesis of hexapyridylbenzene

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Is the thermosalient effect without phase transition possible?

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Routine measurements, such as evaluation of the crystals' habit under hot-stage microscope, can become very thrilling if the crystals suddenly start to jump around as if dancing to some inaudible music. Thermosalient materials are the ones that during heating/cooling undergo an energetic polymorphic phase transition which is so sudden and abrupt that the crystals are ballistically projected to heights of several hundred times larger than their own dimensions. Such single crystals provide an impressive display of the conversion of thermal energy into mechanical work and are thus excellent candidates for the production of active machines, such as "smart" medical devices or implants, artificial muscles, biomimetic kinetic devices, electromechanical devices, actuators and heat-sensitive sensors [1-2].

Our latest study shows a new kind of thermosalient effect in scopolamine bromide. As in most thermosalient systems, uniaxial negative thermal expansion seems to be the most likely candidate for the driving force behind this phenomenon. But one thing in which scopolamine bromide differs from other reported thermosalient materials is the absence of phase transition. In all the other thermosalient systems, thermosalient effect is explained by the accumulation of stress in the crystal lattice which is explosively released during the instantaneous phase transition thus causing the crystal locomotion.

As a comparison, results of the study of thermosalient behavior of oxitropium bromide are presented as well. These two systems have very similar molecular structures, the only difference being that one ethyl group is replaced by methyl group in the case of scopolamine bromide. Both compounds have medical uses, oxitropium bromide is used as a bronchodilator, whereas scopolamine bromide used to prevent nausea and vomiting caused by motion sickness. They also both exhibit thermosalient effect. And this is where the difference stops. As already mentioned, In the case of oxitropium bromide thermosalient effect is caused by the topotactic phase transition during which unit cell drastically changes. On the other hand, surprisingly, scopolamine bromide does not seem to show any phase transition at all, but yet, its crystals are also joyfully jumping around during the heating or cooling of sample.Thermosalient effect is definitely propelled by different mechanisms in these two systems, thus demonstrating and confirming the full complexity and mystery of this phenomenon.

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Acknowledgement

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Thermosalent Behavior on the Dehydration of Scopolamine Bromide Hydrate

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The thermosalient (TS) effect is a property of some compounds which release mechanical stress during variation temperature studies. This can be apparent as rotation, translation, breaking, shape changing or jumping [1,2]. The jumping of a crystal is the most striking aspect of the TS effect and can propel the crystal to a distance up to one meter [3]. As far as we know the number of compounds which show TS behaviour is limited to a few dozens [1]. Beside the movement, TS compounds show other common properties such as i) crystallinity; ii) negative thermal expansion for at least of one of the cell parameters; iii) and a phase transition concomitant with a sudden change of cell parameters [1]. A study of the thermomechanical properties of hydrated scopolamine methyl bromide is presented in this work. The compound crystallizes in the monoclinic space group $P2_1$ at 299(2) K: a = 6.7858(2), b = 11.0084(3), c = 12.6931(3), β=96.025°, Å, V = 942.25(4) Å^3, Z =4. By determination of the crystal structure at various temperatures, the variation of the cell parameters was surveyed. As the temperature rises, the crystal shows a slight contraction on the b, c and V parameters (<1% between 25 and 45 °C) and partial release of the water content. Between 45 and 55 °C, there is a large step on the variation of the cell parameters (Δa=6.1%, Δb=-0.4%, Δc=-8.6%, ΔV=-3.1%) to a cell with parameters a = 7.2118(2), b = 10.9364(3), c = 11.5159(3) Å β=92.75°, V = 907.23(4) Å^3, with total release of the remaining water content.

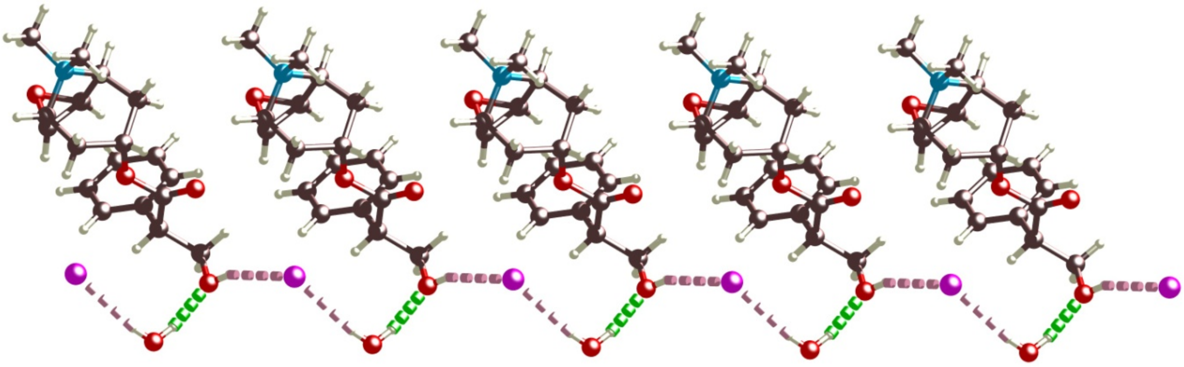

Figure 1: A fragment the hydrated form crystal structure. An infinite chain of hydrogen bonding is broken with the release of water, and accomodation of the bromide anion provoking the TS effect.

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Acknowledgement

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Preparation and Characterization of Cycloadducts with 3,9-Dioxatricyclo[5.2.2.$0^{2,6}$]undec-10-ene-4,8-dione Skeleton

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3,9-Dioxatricyclo[5.2.2.$0^{2,6}$]undec-10-ene-4,8-dione (**1**) framework is of high importance as a potential synthetic intermediate since it possesses a plethora of different reactivity patterns. Therefore, it is of great interest to prepare its derivatives in as straightforward manner and with as high atom economy as possible. One of the most attractive pathways is via Diels–Alder cycloadditions [1], including the possibility between suitably substituted 2*H*-pyran-2-ones and furan derivatives [2]. However, this approach is often unsuccessful: either the cycloaddition partners lack the necessary reactivity to yield the cycloadduct or the reaction conditions necessary for the reaction to proceed are too harsh and the ensuing 3,9-dioxatricyclo[5.2.2.$0^{2,6}$]undec-10-ene-4,8-diones (**1**) do not survive. Namely, the greatest obstacle being the propensity for the system **1** to eliminate a molecule of carbon dioxide via a retro-hetero-Diels–Alder reaction [3] therefore forming benzofuran-2(3*H*)-one (**2**) core that is far less interesting.

One of the possibilities explored previously for the preparation of systems **1** was the application of conventional reflux conditions in methanol with 2-methoxyfuran as the dienophile. However, this approach necessitated rather long reaction times (7–15 h) and the yields were low (45–70%) [2]. Furthermore, in many cases no conversion was observed or an undefined mixture of decomposition products was detected. In some cases addition of methanol to the double bond of the furan ring was also observed, further complicating the reaction outcome. On the other hand, application of high-pressure conditions (13–15 kbar) at room temperature enabled the preparation of a few novel compounds of the type **1** and in one case even the correct stereostructure was determined on the basis of single-crystal X-ray diffration analysis [2]. The details of the synthesis and structural elucidation will be presented.

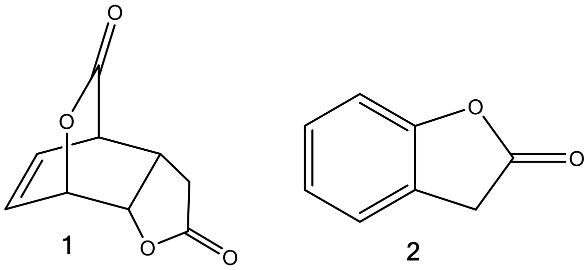
1
2

Figure 1: 3,9-Dioxatricyclo[5.2.2.$0^{2,6}$]undec-10-ene-4,8-dione (**1**) and benzofuran-2(3*H*)-one (**2**) frameworks.

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Iodoform – a forgotten halogen bond donor

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Iodoform (CHI_3) was one of the first halogen bond donors used for preparation of halogen bonded binary solids. It was one of halogen bond donors used by Odd Hassel in his seminal research of charge-transfer compounds during the early 1950-es. [1,2] However, since the renaissance of halogen bond in 1990-es, very little attention was given to iodoform, so that its potential for crystal engineering has for the most part remained unknown. We have therefore decided to study the potential of iodoform as a halogen bond donor by preparing a series of cocrystals of iodoform with a wide range of neutral and ionic halogen bond acceptors.

With neutral ditopic electron donors such as 4,4'-bipyridine and 1,4-diazabicyclo[2.2.2]octane iodoform was found to form cocrystals of 1:1 stoichiometry. In those cases iodoform is donor of two halogen bonds to two acceptor molecules, with the third iodine atom participating only in interhalogen (I···I) contacts. An attempt to prepare an equivalent structure with *N*,*N*,*N*’,*N*’-tetramethylethylenediamine (temed) however yielded a somewhat unexpected cocrystal of iodoform with iodide salt of monoprotonated temed, with the iodide formed by decomposition of iodoform. The structure is characterized by a diamantoid network of iodoform molecules and iodide ions with each iodide acting as an acceptor of three halogen and one C–H···I hydrogen bond from four separate iodoform molecules, with disordered cations filling the space within the network. This has prompted us to study the cocrystallisation of iodoform with organic iodides in more detail. We have found that iodoform forms cocrystals with many organic iodides such as *N*-methyl-3-methylpyridinium iodide, *N*-methyl-3-chloropyridinium iodide, *N*-methyl-3-bromopyridinium iodide, *N*-methyl-3-iodopyridinium iodide, *N*-methyl-4-methylpyridinium iodide, *N*,*N*,*N*,*N*’,*N*’,*N*’-hexamethylethylenediamonium diiodide, *N*,*N*’-dimethyl-1,4-diazoniumbicyclo[2.2.2]octane diiodide and *N*-methyl-2,4,6 trimethylpyridine iodide. In all those cocrystals, the iodide anion acts as halogen (and occasionally C–H···I hydrogen) bond acceptor forming halogen bonded anionic networks, the geometries and topologies of which are determined by the steric properties of the organic counterion.

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Molecular Structure of Heteroleptic Ruthenium(II) Complex Containing a Bidentate Bispyridyl-pyrimidyl Ligand

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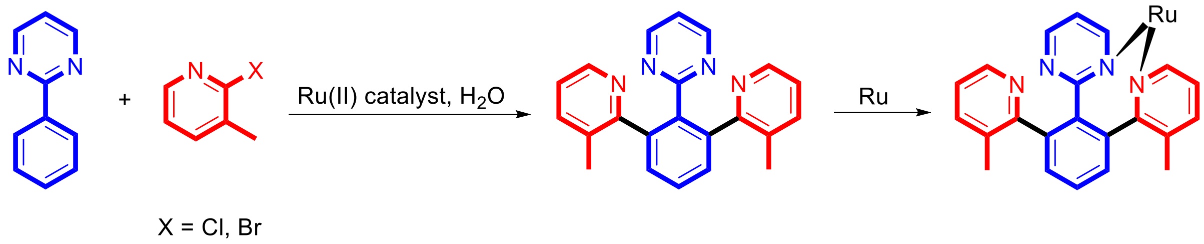
A wide range of polypyridine complexes with transition metals, particularly with ruthenium have been studied over the last few decades due to their versatile applicability. These types of complexes were successfully used as photosensitizers in dye-sensitized solar cells as well as in photoredox catalysis [1]. One of the most fascinating and widely studied properties of polypyridine transition metal complexes is a luminescence, and $[Ru(bpy)_3]^{2+}$ was the first bipyridyl complex where it was observed [2].

In our previous work, we have shown that a ruthenium-carboxylate catalytic system could be used for selective *ortho*-arylation of phenylpyridines, phenylpyrimidines and quinazolines [3]. Herein we report an efficient synthetic approach toward potential multidentante ligands, based on C–H activation/functionalization of 2-phenypyrimidine. The reaction was performed in the presence of ruthenium(II) catalyst in water as a green solvent under microwave irradiation. In this manner, we prepared multiheteroaryl-substituted benzenes mainly containing nitrogen heterocycles (pyridine, pyrimidine,...), which can serve as ligands in coordination to selected transition metals. Molecular structure of one example of ruthenium(II) complex with mixed pyridine-pyrimidine-based ligand will be presented.



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ADVANCES IN X-RAY CRYSTALLOGRAPHY

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Rigaku Oxford Diffraction formally commenced operations on the 29th April, 2015 and is now successfully operating for over three years. With the formation of the new organisation, the widest range of X-ray sources and X-ray area detectors are available. The clear objective is to build upon all existing technologies and the expertise of the earlier Rigaku and Oxford Diffraction entities to achieve optimal solutions covering all applications of crystallography: in chemical, biological, physical, mineralogical, and materials science structural applications. The first incarnation of this was our all new XtaLAB Synergy instrument platform: which will be reported upon.

The range of instrument configurations will be summarised, and illustrated with a number of particular example applications.

As a complement to the crystallography instrument hardware, the data-collection software is fundamental to the achievement of best data quality, along with proper instrument calibration. The newest version of the CrysAlis^{Pro} software suite features the support of a number of Rigaku instruments (the XtaLAB Pro, XtaLAB mini and others based on AFC goniometers). Hybrid Photon Counting (HPC) pixel X-ray area detectors are now supported with the new HPCAD-IMS, a pipeline giving automatically optimal operating conditions for pixel detectors. Improved hard and software allow the highest speed data acquisition. Multi-threaded data acquisition and data reduction pipelines allow fast concurrent data reduction. The ‘What Is This?’ tool gives chemical connectivity information: typically in less than 1min. AutoChem3.0 offers a fine tuned structure completion algorithm and integrates the latest structure solution and refinement tools. AutoChem3.0 also includes a new structure visualizer called ‘StructureExplorer’. StructureExplorer is closely linked with AutoChem3.0 and the Olex2 program: offering the user easiest handling of the structure, from solution to report.

Structural Evidence for Molecular Saccharin Embedded in Ionic Saccharinates of Rubidium and Cesium

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Saccharin is a cyclic sulfimide whose sodium salt is one of the most commonly used artificial low-calorie sweeteners, and is also the main sugar substitute in the diabetics' diet. It is readily deprotonated in solution and affords solid ionic salts or coordination compounds with transition metals where its saccharinate ion displays a wealth of coordination modes. Previously it has been spectroscopically evidenced that saccharin molecules are embedded in the ionic cesium saccharinate. Here we report the structural evidence about two examples of ionic cocrystals of molecular saccharin where saccharin exists as a neutral species and an ion in the same crystal. Namely, with rubidium and cesium cations, saccharin forms isomorphous solid hemihydrate salts, whereas when saccharin is supplied in excess to the reaction mixture, neutral saccharin molecules are stoichiometrically incorporated in both crystals and stable isomorphous ionic cocrystals are obtained. The formation of ionic cocrystals is unprecedented, and adds a new aspect to the rich crystal chemistry of the artificial sweetener.

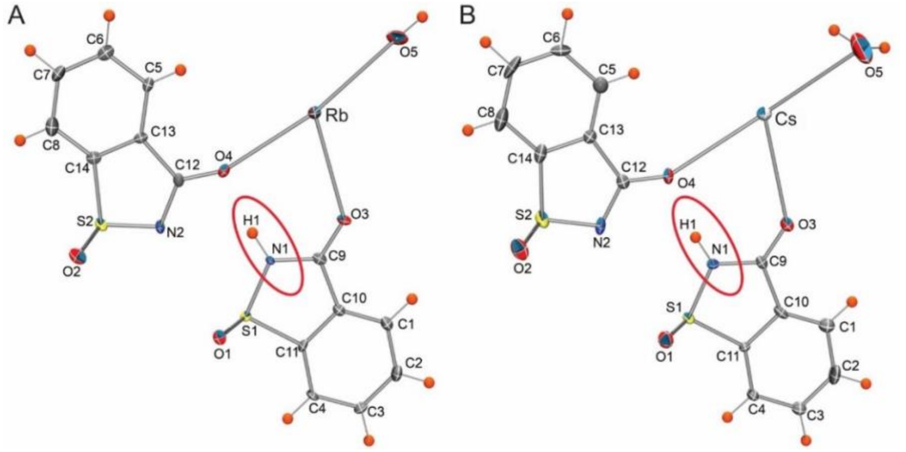

Figure 1. ORTEP of crystal structure of (A) Rb(sac)(Hsac)·H_2O and (B) Cs(sac)(Hsac)·H_2O drawn with 50% ellipsoidal probability with the atom numbering scheme.

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Transport of glutamate in archaea and eukaryotes

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Glutamate transporters catalyse the thermodynamically unfavourable transport of anionic amino acids across the cell membrane by coupling it to the downhill transport of cations. This coupling mechanism is still poorly understood, in part because the available crystal structures of these transporters are of relatively low resolution. In this contribution I will present the crystal structures of the archaeal transporter GltTk in the presence and absence of aspartate resolved to the highest up to date resolution [1, 2], and will report results of molecular dynamics simulations and binding assays to show how strict coupling between the binding of three sodium ions and aspartate takes place.

Furthermore, I will present the latest results, including Cryo-EM structure of a mammalian homologue, which has revealed a few very interesting peculiarities when compared to archaeal homologues.

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Intermolecular interactions in two cyclic amidino-derivatives built three-dimensional network

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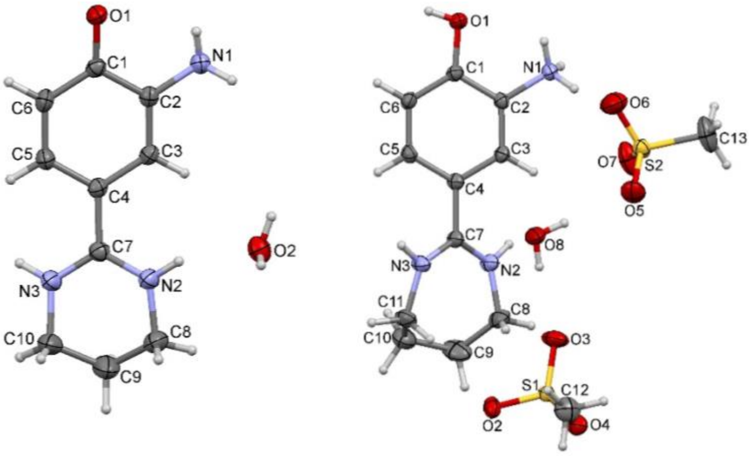
In contrast to a great number of biologically active amidino-substituted benzimidazole and benzothiazole derivatives, benzoxazoles are still rare. The main reason is the lack of a general method for their preparation, which could be based on a condensation reaction of the amidino-substituted 2-aminophenols with aldehydes, carboxylic acids and carboxylic acid derivatives as commercially available substrates. In our last contribution, we presented synthesis of unsubstituted, *N*-substituted and cyclic amidino-derivatives [1]. Herein we present crystal structures of two new cyclic amidino-derivatives of 2-aminophenols as the key building blocks for the synthesis of amidino-substituted benzoxazoles.

Structures of two cyclic amidino-derivatives are shown in Figure 1. Compound **1** crystallized as monohydrate in zwitterionic form with equal C7–N2 and C7–N3 bond lengths, typically for amidino moiety. Crystals of compound **2**, which also crystallized as monohydrate, were obtained in the methanesulfonate salt form, but not as zwitterion. Nitrogen N1 atom in this compound is protonated, and therefore there are two methanesulfonate anions in the structure. As in **1**, amidino moiety is confirmed by almost equivalent C7–N2 and C7–N3 bond lengths. Supramolecular structures of **1** and **2** contain a number of various intermolecular interactions (O–H···O, N–H···O, O–H···N and C–H···O hydrogen bonds, as well as C−H···π and π···π interactions) that built three-dimensional network.



(a) b)

Figure 1. Molecular structures of (a) 2-amino-5-(3,4,5,6-tetrahydropyrimidin-1-ium-2-yl)phenolate hydrate (**1**), and (b) 2-(3-amino-4-hydroxyphenyl)-4,5,6,7-tetrahydro-1*H*-1,3-diazepin-3-ium methanesulfonate hydrate (**2**), with the atom numbering scheme.

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Revealing the structure of the first plant aminoacyl-tRNA synthetase at 2.3 Å

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In the process of protein translation, a proper attachment of a cognate amino acid to the appropriate tRNA requires involvement of an aminoacyl-tRNA synthetase (aaRS). Outside translation, aaRSs may exert additional non-canonical activities in diverse cellular processes. Eukaryotes and the majority of prokaryotes (with an exception of a small number of methanogenic archea) possess bacterial type of seryl-tRNA synthetase (SerRS). SerRSs are homodimers that contain a globular catalytic domain catalyzing aminoacylation and a coiled-coil tRNA binding domain needed for recognition of cognate tRNA. Even though many crystal structures of bacterial type of SerRS are known, no plant structure of SerRS was solved untill now.

Here we report the first crystal structure of plant SerRS from *Arabidopsis thaliana* (*At*SerRS) at the resolution of 2.3 Å. This is also the first crystal structure of plant aaRS. The protein crystallized in the monoclinic *I* 2 space group with one monomer per asymmetric unit. The final model of *At*SerRS structure was refined to the values of $R_{work} = 0.211$ and $R_{free} = 0.278$. The monomer is composed of two domains, the tRNA binding domain and the catalytic core, well conserved among the other bacterial types of SerRS. A dimer is generated by the two-fold symmetry axis. It forms a dimer also in the solution as confirmed by SLS. Very flexible parts of the molecule lack electron density so the amino acids residues comprising Glu10-Gly12, Lys67-Ala73, Ala214-Asp220, Ser274-Thr279, Gly378-Glu384 and 437Ala-456Glu are not visible in the crystal structure. Interestingly, a unique disulphide bond between Cys213 and Cys244 of the same monomer is present in the crystal structure.

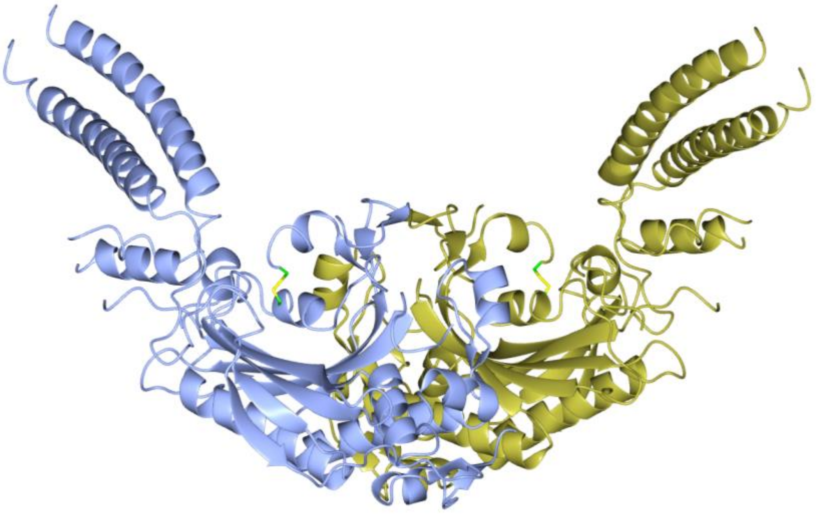

Figure 1: Dimer of SerRS from *Arabidopsis thaliana* (monomer A in blue and monomer B in gold color). Disulphide bridge is highlighted in yellow.

Halogen-bonded cocrystals of an imine derived from *N*-aminomorpholine and 4-nitrobenzaldehyde: a playground for halogen bonding

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Imines derived from *N*-aminomorpholine and aromatic aldehydes are potentially good building blocks in crystal engineering of halogen-bonded materials [1,2]. Herein we have synthesized an imine (**1**) from 4-nitrobenzaldehyde and *N*-aminomorphline that has various functional groups which can act as halogen bond acceptor sites: morpholine oxygen atom, morpholine nitrogen atom, nitro group oxygen atom, imine nitrogen atom and the phenyl π-system [3]. For cocrystal synthesis, as halogen bond donors, we have selected perfluorinated compounds of different geometries based on iodine: 1,4-diiodotetrafluorobenzene (**14tfib**) and 1,3,5-triiodotrifluorobenzene (**135tfib**). We obtained two cocrystals by mechanochemical and solution based synthesis. Products were characterized by means of powder X-ray diffraction, differential scanning calorimetry (DSC) and by single crystal X-ray diffraction.

In the (**1**)$_2$(14**tfib**) cocrystal only the bifurcated I···O$_2$N halogen bond is present (d(I···O) = 3.217 Å, ∠(C–I···O) = 169.4°; d(I2···Cl1) = 3.439 Å, ∠(C–I···O) = 153.2°), leading to the formation of a discrete halogen bonded complex. These discrete complexes are then connected into a layer through paired C–H···O hydrogen bonds, and through C–H···F contacts. Unexpectedly, the morpholinyl fragment does not participate in any directional supramolecular interactions. On the other hand, in the (**1**)(**135tfib**)$_2$ cocrystal, a 1:2 stoichiometry of **1** and **135tfib** is present (Figure 1). The two crystallographically independent **135tfib** molecules exhibit different supramolecular bonding. The first **135tfib** molecule participates in halogen bonding as a tritopic donor forming I···N$_{\text{imine}}$, I···O$_{\text{morpholine}}$ and I···I halogen bonds (d(I···N) = 3.288 Å, ∠(C–I···N) = 171.9°; d(I···O) = 3.066 Å, ∠(C–I···Cl) = 170.4°; d(I···I) = 3.904 Å, ∠(C–I···Cl) = 163.0°). The second crystallographically independent **135tfib** molecule participates in halogen bonding as a ditopic donor, forming I···O$_{\text{nitro}}$ and I···C$_{\pi}$ halogen bonds (d(I···O) = 2.941 Å, ∠(C–I···O) = 174.4°; d(I···C) = 3.381 Å, ∠(C–I···C) = 172.1°)as well as being an acceptor in type II halogen bonding. The combination of the mentioned halogen bonds gives rise to an intricate 3-D network.

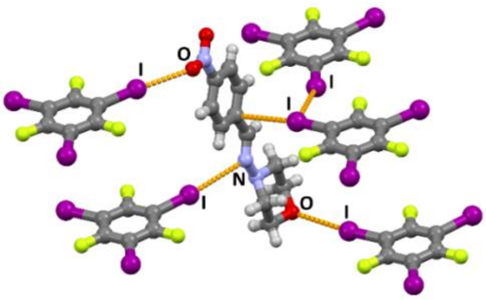

Figure 1: Fragment of the crystal structure in (**1**)(**135tfib**)$_2$.

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Two-electron multicentric covalent bonding: how many centres?

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Charge density was studied for three model systems with strong interactions bordering intra- and intermolecular: hydrogen bonding, halogen interactions and π-stacking. Our studies revealed that in all three cases the interaction involves multicentric two-electron covalent bonding.

Nature of the strong hydrogen bond was studied on the well-known Zundel cation [1]. It has long been known that the strongest hydrogen bonds are in fact weak covalent 2-electron/3-centre bonds of order 0.5; our study indicated that the proton donor and acceptor can't be distinguished. Both O-H bonds have a maximum electron density of *ca*. 1 e Å^{-3}, and the negative Laplacian indicates a dominantly covalent interaction.

It is quite well known that hydrogen and halogen bonding are similar, and recent studies showed that they are also similarly strong [2]. In a halogen bond *D*-X···*A* the covalent bond *D*-X is elongated and the halogen is displaced towards the acceptor. Therefore we studied three systems with varying strenght of the halogen bond. Pure *N*-bromosuccinimide was used as a standard, to evaluate charge density of an unperturbed N-Br bond. In a co-crystal of *N*-bromosuccinimide with 3,5-dimethylpyridine, the Br atom is displaced towards the acceptor by almost 0.4 Å and the maximum electron density in the "intermolecular" Br···N contact is 0.4 e Å^{-3}, indicating a significant covalent contribution. The strongest halogen bond was studied on a bromonium ion, whose central N-Br-N fragment is in fact a two-electron/three-centre covalent bond.

π-stacking of planar radicals involves spin coupling and mixing of SOMO orbitals, so it also has a considerable covalent character. Our studies of semiquinone radicals involved three types of contact: closely interacting radical dimers (known as 'pancake bonding') [3], trimers of partially charged rings [4] and stacks of equidistant radicals [3]. X-ray charge density and quantum chemical modelling showed significant covalent contribution in all of them. Therefore, 'pancake bonding' can be regarded two-electron multicentric covalent bonding. Apparently, covalent bond can also be unlocalised.

Acknowledgements

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Computational study of hydrogen bond in systems of selected acetylacetonato complexes of Cu^{II} – theory *vs.* experiment

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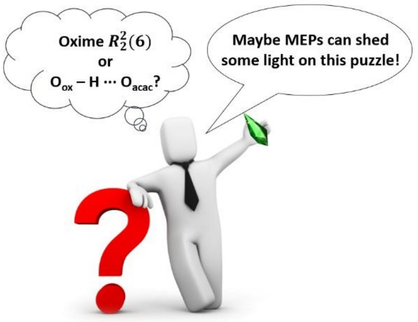
Delivering crystalline solids with desired supramolecular assembly and chemical composition is still one of the main challenges that crystal engineering community deals with. [1] That is especially true for systems that contain multiple hydrogen bond acceptor sites, as the number of possible hydrogen bonds in these systems increases. However, by modifying certain features, such as electron density in a close proximity of potential hydrogen-bond donors and/or acceptors (by, for example, introducing electron-withdrawing or donating group), it is possible to influence molecular self-assembly of the system and accomplish the targeted synthon even in those settings. [2] Calculated molecular electrostatic potential (MEP) values have recently gained substantial attention as a practical tool in rationalization of supramolecular outcome of systems with multiple hydrogen-[3] and halogen-bond[1] donors and acceptors. There are also several reports on their application even for the prediction of supramolecular synthetic events of purely organic systems.

As a part of our broader research goal that is directed towards deriving robust and reliable supramolecular synthetic strategies for assembling metal-organic systems in more predictive way, we have delivered and structurally characterised a series of hexafluoroacetylacetone (**hfac**) and trifluoroacetylacetone (**tfac**) complexes of Cu^{II} with selected pyridine-based oximes (4-pyridinealdoxime, 4-**Hoxpy**; 4-acetylpyridineketoxime, 4- **Meoxpy**; 3-pyridinealdoxime, 3-**Hoxpy**; 3-acetylpyridineketoxime, 3-**Meoxpy).** Although the transferability of the self-complementary oxime synthon (6), from purely organic to metal-organic systems proved to be possible, the competing hydrogen-bond acceptors residing on the *ß*-diketonato ligands are still staying in the way of a reliable delivery of targeted supramolecular outcome.

Here, we are presenting rationalization of the structural data against the backdrop of MEPas a step forward, towards the supramolecular synthesis of metal-organic systems.



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Isotropc, linear particle growth and the parallelbody set problem in SAS

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The contribution analyzes a long standing problem in the field of particle growth. Small-angle scattering (SAS) experiments describe nanoparticles. This includes particle growth processes. There exist different approaches in this field. From a geometrical point of view - at least - two limiting cases A and B are of practical interest.

A. Linear particle growth means that the initial particle X_0 isotropically increases by a constant length factor in all directions.
B. The particle X_0 increases by the same distance length ρ over the whole surface.

Let S_0, V_0 and $g_0(r)$ be the starting surface area, starting volume and starting SAS correlation function (CF) of a particle, respectively. In case A, the new parameters result via $S_1=S_0\ \mathrm{const}^2$ and $V_1=V_0\ \mathrm{const}^3$. For example, in the case of an ellipsoid with semi axes $\{a_0, b_0, c_0\}$, the increased semi axes $\{a_1= a_0\ \mathrm{const}, b_1= b_0\ \mathrm{const}, c_1=\mathrm{const}\ c_0\}$ follow. The volume $V_1=\mathrm{const}^3\ V_0$ results. The SAS CF of the proportionally increased ellipsoid with largest particle diameter $L_1=2c_1$ is given in terms the starting CF $g_0(r)$ by $g_1(r) = g_0(r\ L_0/L_1)$.

However, in case B, a general solution for the CF $g_1(r, \rho)$▯of the parallelbody (parallel set X_ρ) in terms of the CF of the initial set X_0 is unknown, see Stoyan D. & Stoyan H., Methoden der Geometrie-Statistik, Akademie Verlag, Berlin 1992, page 152. Here, the variable length ρ, $0\leq\rho<\infty$, denotes the radius of a sphere, the center of which continuously moves along the particle surface, see figure 1.

In stochastic geometry, the parallel set X▯▯to a given set X_0 has been subject of intense investigations. It writes $X_\rho=X \oplus B(\rho)$. In fact, analytic solutions have been found in the ellipsoid case. This includes the mean caliper diameter H of this body. For general formulas of H, see (Weibel R.E., Stereological methods. vol. 2, Theoretical foundations, Academic press, London 1980, page 154). Furthermore, there exist connections between H and the CFs $g_0(r)$ and $g_1(r, \rho)$ of the parallelbody.

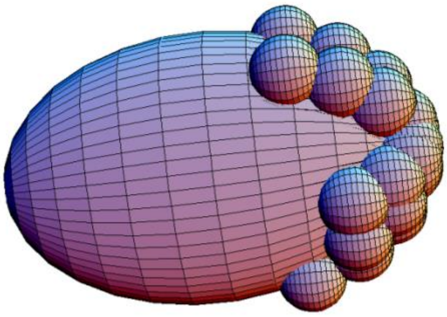

Figure 1: Illustration of the construction of the parallelbody X_ρ of an ellipsoid X_0. The resulting particle is limited by the envelope of all the outer border limits of the covering spheres of radius ρ. If ρ increases more and more, a huge sphere of volume $V_\rho = (4/3)\ \pi\ \rho^3$ results. Then, it is a complicated task to reconstruct the initial particle.

Halogen Bonding in Halogenopyridinium Hexacyanoferrates

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Hexacyanoferrates (**hcf**) are well known to form metal-organic frameworks, (Prussian blue analogues) by coordination to metal atoms or acting as hydrogen bond acceptors. Recently, however it has been demonstrated that a new class of **hcf**-based materials by using partly protonated **hcf** anions which assemble *via* direct hydrogen bonding of the anions into chains, 2D or 3D networks of the protonated **hcf** species, with 2D networks of hydrogen bonded H_2**hcf**$^{2-}$ anions being the most common motif.[1]

It has been shown that the exact mode of the assembly of **hcf** species can be tuned by the strength (pK_a value), steric properties, or the amount of the base.[1] However, in principle this should also be achievable through modification of the ability of the base to form additional interactions with the **hcf** anions. In order to examine this, we have ventured to study **hcf**-s of halogenpyridines, which can act as halogen bond donors (with **hcf** cyano groups as halogen acceptors [2]). Comparing the structures within a series of halogenpyridines – *meta*- (3-chloropyridine, **3-Clpy**; 3-brompyridine, **3-Brpy**; 3-iodopyridine, **3-Ipy**) or *ortho*- (2-chloropyridine, **2-Clpy**; 3-brompyridine, **2-Brpy**; 2-iodopyridine, **2-Ipy**), allowed us to isolate the effect of halogen bond on the structure of the formed, as the pK_a values as well as molecular shapes within a series is almost identical, and the only significant difference is the ability of the pyridine to form halogen bond (increasing with the size of the halogen).

Crystallisation of the *meta*-halogenpyridines with hexacyanoferric(II) acid (H_4**hcf**) yielded structures containing H_2**hcf**$^{2-}$ anions. The two stronger halogen donors, **3-Brpy** and **3-Ipy**, yielded isostructural compounds with hydrogen bonded chains of anions bridged by water molecules and cations bridging between the chains by forming a hydrogen bond with one chain and halogen bond with the other. Weak halogen donor, **3-Clpy** yielded a 2D network of hydrogen bonded H_2**hcf**$^{2-}$ anions with **3-ClpyH**$^+$ cations bonded to the networks through hydrogen bonds only. *Ortho*-halogenpyridines on the other hand formed three different structures, with **2-Clpy** and **2-Brpy** forming hydrogen bonded 3D-netwotks (latter of directly bonded H_3**hcf**$^-$ anions, and former of **hcf**$^{4-}$ anions bridged by H_3O^+ cations), pyridinium cations and neutral pyridine molecules filling the space within the network without participating in either hydrogen or halogen bonding with the **hcf** network. Conversely, **2-Ipy**, being the strongest halogen bond donor, binds to the anions both through hydrogen and halogen bonds, thus disrupting the 3D network and forming 2D networks of H_2**hcf**$^{2-}$, heavily distorted by the halogen bond. For comparison, when **4-Ipy** was used 2D networks of H_2**hcf**$^{2-}$ also formed, however now they were regular in spite of **4-Ipy** being a halogen bond donor, as the halogen bonding in this case did not bend a hydrogen bonded network, but rather interconnect neighbouring networks.

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Cocrystalization of halogenide salts of organic bases with 1,4-diiodotetrafluorobenzene

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Halogen bond is intermolecular short-range interaction that plays a significant role in crystal packing and is therefore of great importance to crystal engineering. Interaction is achieved between a molecule with a partially positively charged halogen atom connected to an electron-withdrawing group (halogen bond donor) and a Lewis base (halogen bond acceptor). With regard to the wide spectrum of organic bases studied to date, halogenide ions are poorly investigated halogen bond acceptors.[1],[2] In this study, with the aim of studying the halogen bonded motifs with halide ions, we attempted to prepare a series of cocrystals of 1,4-diiodotetrafluorobenzene (**1,4-tfib**) with halogenides of several nitrogen bases.

Halogenide salts were prepared by addition of hydrohalic acids in ethanol solution of a nitrogen base, whereupon precipitation of the product immediately started. Cocrystals were obtained by dissloving corresponding salt and **1,4-tfib** in ethanol. A number of crystallization experiments yielded crystals of sufficient quality for diffraction experiments and molecular and crystal structures of cocrystals have been determined. In prepared compounds, **1,4-tfib** and halogenide ions were linked in zig-zag chains with C–I⋯X^- halogen bonds, while organic cations were hydrogen bonded to the halogenide ions through N–H⋯X^- hydrogen bonds. It is interesting to note that in the case of 2,4,6-trimethylpyridinium bromide there was one hydrogen bond of type N–H⋯Br^- for every bromide and organic cation, whereas in the case of iodide of the aforementioned cation, the N–H⋯I^- hydrogen bonds were bifurcated, interconnecting pairs of iodides belonging to adjacent zig-zag chains.

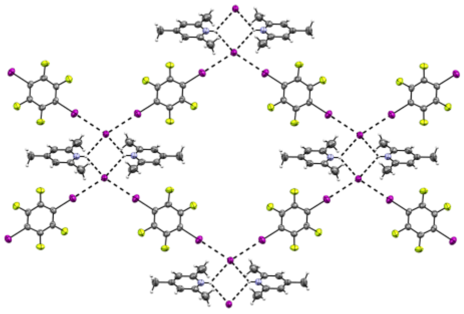

Figure 1. ORTEP-representation of the crystal structure of (**kolHI**)(**1,4-tfib**)**.** Displacement ellipsoids are drawn at the 50 % probability level.

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Can MEPs obtained from DFT calculations be used to a priori determine the effectiveness of the employed supramolecular strategies?

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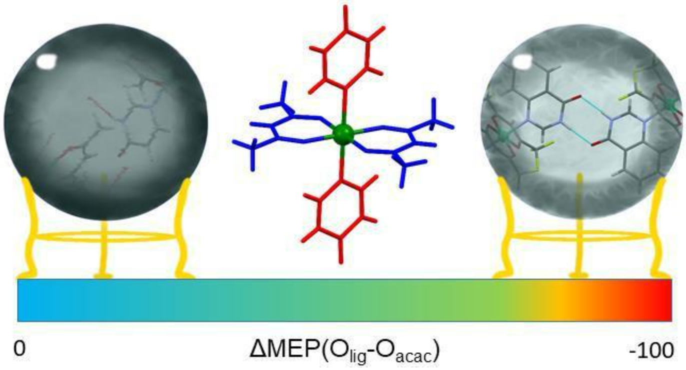
Crystal engineering as an interdisciplinary science with the aim of obtaining desired structural topologies and material properties in the solid-state envelops many different fields of research. In the last ten years computational chemistry has been getting more and more applications in crystal engineering and the study of molecular electrostatic potentials is showing great promise as a useful tool to rationalize and even predict observed synthons for both halogen[1] and hydrogen[2] bonds. However, research in the metal-organic setting and all of its potential properties unlocked by employing metal centers still needs to be furthered and we believe that computational methods will prove to be invaluable to extend our understanding of these systems. The question remains, can we use in-silico methods to a priori determine the outcome of employed strategies for supramolecular synthesis in the metal-organic setting?

In an attempt to answer this conundrum we have opted to obtain 1-D supramolecular chains in the metal-organic solid state using the $R^2_2(8)$ synthon formed by lactam groups. β-diketonato complexes of Co^{II}, Ni^{II} and Cu^{II} with pentane-2,4-dione and hexafluoropentane-2,4-dione were used as starting building blocks and pyrimidin-4-one and quinazolin-4-one were used to introduce the lactam groups. A total of ten compounds were prepared employing different ligands to ensure that we have a sufficiently large set of crystal structures to adequately test our hypothesis. Molecular electrostatic potentials calculated via DFT methods on generated geometries were used in an attempt to predict the supramolecular outcome of our synthesis. In all but two cases the analysis of the difference between MEP values on β - diketonato and lactam oxygen atoms enabled us to postulate that the formation of supramolecular synthons between lactam groups is favored. The obtained crystal structures were in accordance with our predictions and in seven out of ten crystal structures $R^2_2(8)$ motifs and in one crystal structure a C(4) motif between lactam groups was observed.



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Structural and DFT study of pyridine and imine nitrogen atoms as halogen bond acceptors: interplay of halogen bonds in the solid state

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As importance of halogen bond in the solid state raises, more and more halogen-bonded cocrystals are synthesized and investigated.[1,2] In many of them polytopic donors and acceptors are used, which often leads to the competition between different halogen bonds.[3] Further, halogen bonds are usually not isolated in the crystals, but rather coexist with other interactions, which leads to some yet unclear effects, mainly related to how one interaction affects the strength of the other.[4,5]

In order to study the competition of pyridine (N_{py}) and imine (N_{im}) nitrogen atoms as halogen bond acceptors, two bis(3-pyridyl)diimines were cocrystalized with three polytopic halogen bond donors: 1,4-diiodotetrafluorobenzene, 1,3-diiodotetrafluorobenzene and 1,3,5-triiodotrifluorobenzene (Figure 1). SCXRD measurements revealed that the pyridine nitrogen atom is the halogen bond acceptor in all six cocrystals, while imine nitrogen atom is acceptor in three of them. Also, in four cocrystals, the C–I···I halogen bond, orthogonal to the C–I···N_{py} halogen bond, was present, having as an acceptor the negative region of iodine atom. The cocrystals and the halogen bonds were characterized by means of quantum-chemical calculations, revealing that the C–I···N_{py} is stronger than C–I···N_{im} halogen bond, both in the gas phase and in the solid state. Also, observed differences in the supramolecular behavior of donors, as well as ambivalent (donor-acceptor) properties of iodine atom in the donor molecules, were elucidated, uncovering so far unseen antagonistic and agonistic couplings between multiple halogen bonds.

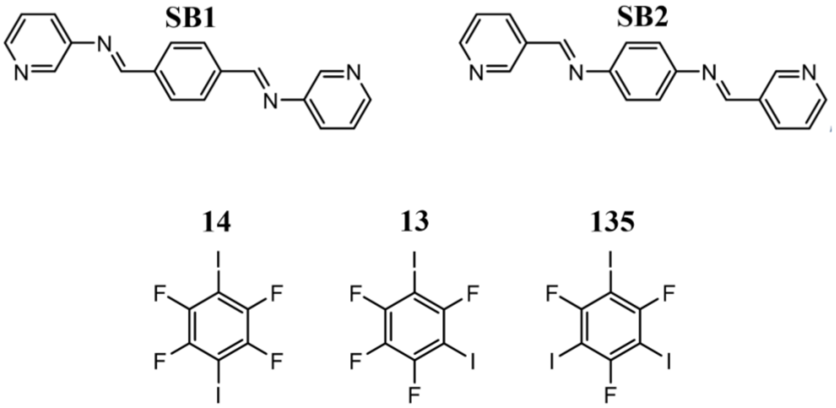

Figure 1: Halogen bond donors (**14**, **13** and **135**) and acceptors (**SB1** and **SB2**) used in this work.

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Synthesis and structure of a new iron(II) coordination compound with isonicotinamide

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Crystalographic data

$(isnH)_2[Fe(isn)_2(SO_4)_2(H_2O)_2]\cdot 2H_2O$, *isn=isonicotinamide*, M_r=794,56, triclinic, *P-1, No.2,* a=6.7949(3), b=8.2550(4), c=14.7654(7) Å, α=74.203, β=87.629, γ=86.644°, V=795.29(6) Å^3, Z=1, D_x=1.659 Mg m^{-3}, CuKα radiation, T=293(1) K, Agilent Supernova diffractometer with Atlas CCD detector, 9301 measured and 3208 independent reflections, R_{int}=0.0316, R=0.0372, wR=0.1015, $\Delta\rho$(max,min)=(0.36,-0.49)) e Å^{-3}.

Isonicotinamide is among the most effectively used co-crystallizing compounds in crystal engineering due to the presence of both pyridyl and amide groups which allow the formation of many hydrogen bond arrangements [1,2]. Orange – brown colored crystals were obtained by the reaction between $FeSO_4\cdot 7H_2O$ and isonicotinamide (molar ratio 1 : 2) under reflux in methanolic solution. The unit cell of the title compound consists of a complex anion containing Fe(II) (octahedrally coordinated by two isonicotinamide ligands, two sulfate ligands and two water molecules), two protonated isonicotinamide cations and two non-coordinated water molecules. The compound was further investigated by FTIR, thermal analysis and magnetic measurements.

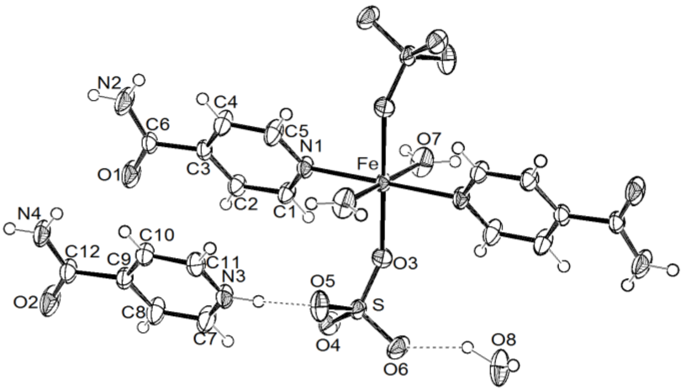

Figure 1: ORTEPIII drawing of title compound, labelled are non-hydrogen atoms of the asymmetric unit

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X-Ray Analysis of Intermediates and Products involved in Solid-State C–H Bond Activation by Pd(II) Chloride Precursors

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C–H bond activation is often the first step in metal-catalyzed functionalization of the organic compounds usually performed using palladium (Pd) catalysts. Number of reports on successful solid state C–H bond functionalization by ball milling is growing, but no deeper insight into their mechanism has been obtained. Recently, a detailed mechanistic study of the solid-state activation of two C–H bonds in an asymmetric azobenzene substrate by Pd(II) chloride precursors, *e.g.* $PdCl_2$ and $PdCl_2(MeCN)_2$, has been elucidated using *in situ* collected Raman spectra and *ex situ* spectroscopic and synthetic experiments. Results support a regioselective two-step reaction in which each step involves a coordination of the substrate to the Pd(II) precursor forming an adduct that then undergoes the C–H bond cleavage.

Herein we report single-crystal X-ray diffraction experiments that allowed for structural identification of the azobenzene reactant as well as reaction intermediates and products of the double C–H bond activation in the solid state (Figure 1). Structural analysis proved as a key step toward determination of the reaction course and supported the proposed mechanism of the C–H bond activation in the azobenzene substrate, which was found analogous to the proposed mechanism for these reactions in solution.

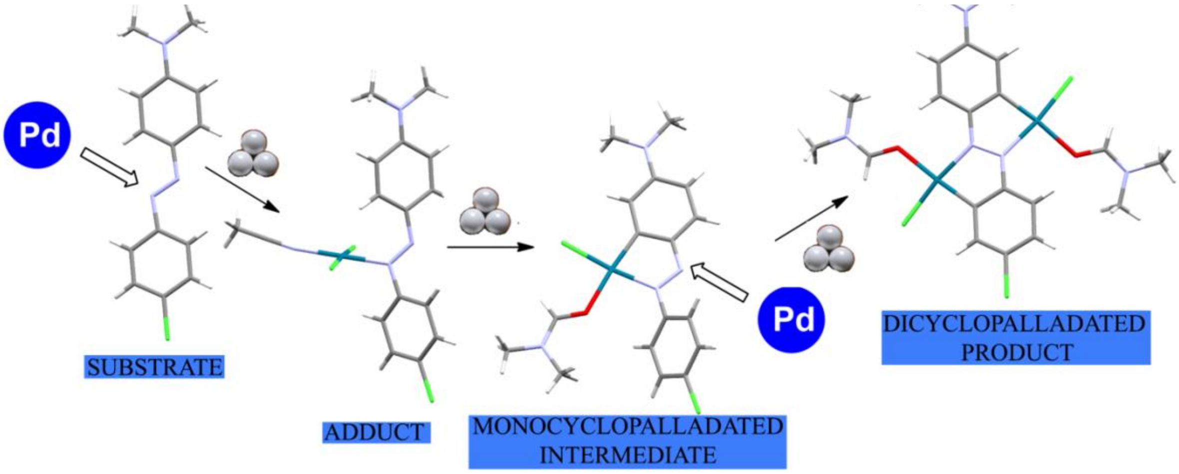

Figure 1: Structurally characterized species involved in double solid-state C–H bond activation in azobenzene substrate by Pd(II) chloride precursors yielding a doubly palladated azobenzene complex.

Supramolecular synthesis of Co^{II} and Ni^{II} complexes with acetylacetonate derivatives and pyridyl oximes

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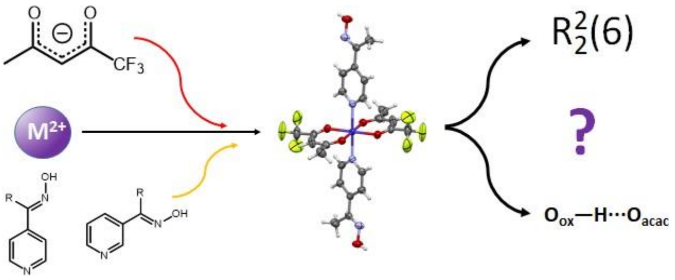
Recently, it has been shown that it is possible to direct the supramolecular assembly in the organic solid state by employing certain supramolecular synthons.[1] However, it still remains to be determined if those strategies are viable in the metal-organic setting due to disruptive effect of the counter-ion present in those surrounding. One of the approaches to tackle this problem is to employ charge-balancing ligands to coordinate to the metal cation thus consequently minimizing their disruptive effect. In our previous work on β-diketonato complexes of Co^{II} and Ni^{II}, we were aiming to connect the metal-containing building blocks via self-complementary hydrogen bond synthons ($R^2_2(6)$ motifs) formed between the oxime groups from neighbouring coordination units. We have shown that the supramolecular outcome is primarily influenced by the acceptor potential of the oxygen atom form β- diketonato ligands, and in all the cases the hexafluoroacetylacetonate ligands, the targeted synthon was obtained. We have also shown that the position of the oxime group on the pyridine ring, accompanied with the electron donating $–CH_3$ groups in the vicinity of the oxime nitrogen atom, can improve the hydrogen bonding acceptor power of the nitrogen atom for the desired synthon to be formed.[2]

In this work, we have set out to determine if we can build upon our previous findings and to obtain the targeted synthons by employing only one $–CF_3$ group, i.e. trifluoroacetlyacetone ligands, and thus gain further insight into the supramolecular potential of the oxime group as a supramolecular linker. We synthesized a series of Co^{II} and Ni^{II} complexes with trifluoroacetylacetone (tfac) and selected pyridine-based oximes (4- pyridinealdoxime, 4-Hoxpy; 4-pyridineketoxime, 4-Meoxpy; 3-pyridinealdoxime, 3-Hoxpy; 3-pyridineketoxime, 3-Meoxpy), and our structural results showed that the targeted self- complementary oxime synthon could be delivered. Here we have also demonstrated that the introduction one $–CF_3$ group to β-diketonato ligands have substantial potential reduction of accepting power of the acac-based oxygen atoms for the desired supramolecular link to occur.



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A solved mystery? A novel zinc(II) ammine complex.

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In continuation of the research on zinc(II) quinaldinate complexes with various nitrogen- and/or oxygen-donor ligands [1], a reaction system of [Zn(quin)$_2$(CH$_3$OH)$_2$] (quin$^-$ = an anionic form of quinoline-2-carboxylic acid) with diethanolamine was investigated. One of the reactions resulted in large colourless crystals. Their infrared spectrum lacked the characteristic features of coordinated diethanolamine in any of its forms. In addition the IR spectrum bore a high resemblance to that of a known and an unwanted product, an aqua complex with the [Zn(quin)$_2$(H$_2$O)] composition [2]. The crystals were subjected to the X-ray structure analysis which revealed a different cell that the one determined for [Zn(quin)$_2$(H$_2$O)]. A second polymorph was thus expected as the most likely solution. Surprisingly, the X-ray structure analysis revealed ammonia coordinated to zinc(II) ion in place of the anticipated water. The [Zn(quin)$_2$(NH$_3$)] formulation of the compound is supported by the bonding pattern within the zinc(II) coordination sphere and the results of the elemental analysis. A detailed analysis of the IR spectrum in retrospective revealed absorption bands that could be ascribed to vibrations of the coordinated ammonia.

Crystal structure of a novel zinc(II) ammine complex will be presented. A likely mechanism of its formation will also be discussed.

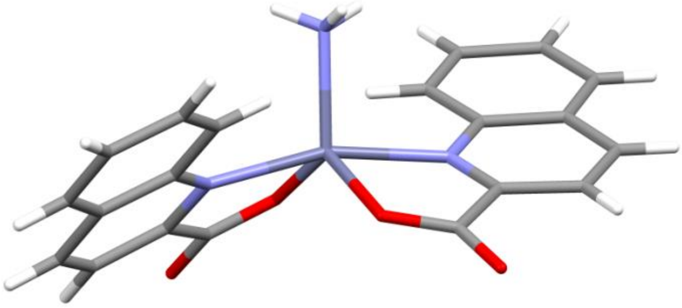

Figure 1: A drawing of a [Zn(quin)$_2$(NH$_3$)] complex molecule.

Crystal data for $C_{20}H_{15}N_3O_4Zn$: monoclinic $P\ 2_1/n$, a = 12.3289(4) Å, b = 9.6117(4) Å, c = 14.9979(6) Å, β = 97.083(3)°, V = 1763.71(12) Å^3, Z = 4, ρ_{calcd} = 1.607 g cm^{-3}, μ = 1.426 mm^{-1}, 10390 reflections collected (4446 independent, R_{int} = 0.0260). The final residues were R = 0.0321, and wR_2 = 0.0714 [3588 reflections, $I > 2\sigma(I)$], and R = 0.0455, and wR_2 = 0.0783 [all data].

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Combined Mechanocemical and solution shyntesis of Copper(II) Carboxylates

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Synthesis of paddlewheel complexes is not demanding and their abbility to bind various ligands makes them eligible building blocks in crystal engineering and preparing metal-organic frameworks. [1,2,3,4].

CSD contains suprisingly small number of non-acetato or benzoato copper(II) paddlewheels. We decided to search for new carboxylato coppr(II) complexes by combining mechanochemical and solution synthesis. Our results are promising and provided us with several single crystal specimens for which we solved their crystal and molecular structures.

Our results indicate a good potential for synthesis of various paddlewheels in situ and corresponingly more targeted multicomponent supramolecular networks that contain metal ions should be obtained

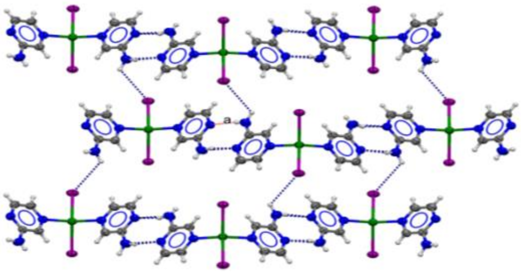

Figure 1: Figure caption (font type Calibri, 10pt).

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Organometallic ruthenium(II) complexes with selected *N,N*-donor ligands – interesting systems where also concomitant polymorphism was observed.

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Nowadays ruthenium complexes are very intensely studied due to their numerous interesting properties, which find various applications in abundant aspects of life (e.g. catalysis; solar cells; potential metal based drugs). In last years our group was dealing with interactions of ruthenium with several biologically active ligands that coordinate to metal ions through different donor atoms (e.g. *O,O*-donor quinolones; *N*-donor azoles; *O,O*-donor diketonates; *N,O*-donor hydroxyquinolines; *O,S*-donor pyrithione). Recently we have also started to work on ruthenium complexes with various *N,N*-donor ligands, such as dimethyl 6-(pyridine-2-yl)pyridine-3,4-dicarboxylate, as potential inhibitors of various enzymes (e.g. aldo-keto reductases [1] and lipoxygenases [2]).

In this talk some representative examples will be presented and the structures of two concomitant polymorphs of a ruthenium organometallic compound will be discussed [3]. Crystal structures have revealed that the most bond lengths in both complexes are approximately the same with differences in methoxycarbonyl groups and in *p*-cymene to the ruthenium central atom orientations. Both structures do not contain classic hydrogen bonds, only weak interatomic interactions were observed.

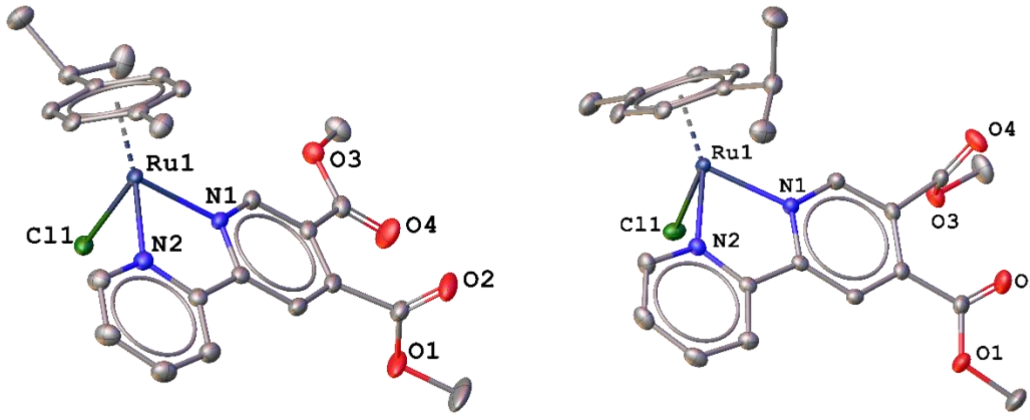

Figure 1: Different orientation of methoxycarbonyl groups and *p*-cymene ligand in the organometallic ruthenium complex that exhibits concomitant polymorphism. The counter-anions have been omitted for clarity.

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Thiosemicarbazides and Thiosemicarbazones as Ligands in Ni(II) Coordination Compounds

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Nickel(II) metal complexes have been synthesized in the reaction of *N*-(pyridin-2-yl)hydrazinecarbothioamide (**1**) [1] or *N*-(6-methyl-pyridin-2-yl)hydrazinecarbothioamide (**2**) with $Ni(NO_3)_2 \cdot 6H_2O$ and KSCN in molar ratio 2 : 1 : 2 in methanol as a solvent. An octahedral complex (**3**·2MeOH) has been crystallographically characterized with the formula [Ni(**2**)$_2$(SCN)$_2$]·2MeOH (Figure 1) where thiosemicarbazide ligands are coordinated without deprotonation to the nickel(II) center.

Thiosemicarbazones and their metal complexes have received considerable attention due to their coordination chemistry and a broad range of pharmacological properties[2]. For this reason we prepared different thiosemicarbazones with the condensation reaction of corresponding **1** or **2** thiosemicarbazides and 2-, 3- or 4-acetylpyridine. In the subsequent reaction between 2-acetylpyridine *N*(4)-pyridylthiosemicarbazone with $Ni(NO_3)_2 \cdot 6H_2O$ and KSCN we obtained complex **4** (Figure 2) where deprotonated thiosemicarbazone ligand is tridentately coordinated to Ni(II) center forming two fused five membered chelate rings.

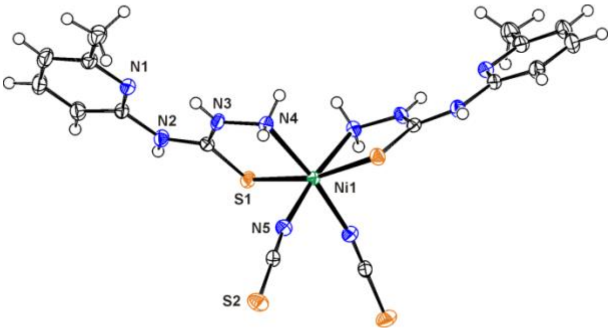

Figure 1: Structure of complex **3**.

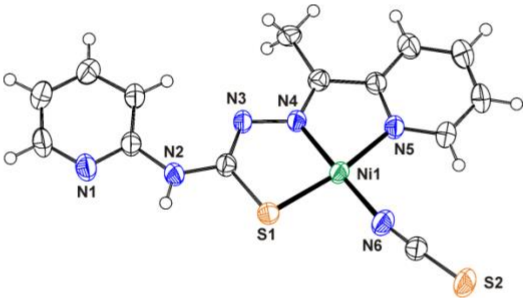

Figure 2: Structure of complex **4**.

Crystal data:

1: $C_{18}H_{28}N_{10}NiO_2S_4$, $M_r = 603.45$, monoclinic, $C\,2/c$, $Z = 4$, $a = 18.5982(7)$, $b = 8.2908(3)$, $c = 16.8855(6)$ Å, $\beta = 96.811(3)°$, $V = 2585.27(16)$ Å^3, R_1 $[I > 2\sigma(I)] = 0.0309$, wR_2 (all data) = 0.0871.

2: $C_{14}H_{12}N_6NiS_2$, $M_r = 387.13$, monoclinic, $P\,2_1/n$, $Z = 4$, $a = 7.2911(3)$, $b = 15.8577(4)$, $c = 13.6761(4)$ Å, $\beta = 90.801(4)$ °, $V = 1581.08(9)$ Å^3, R_1 $[I > 2\sigma(I)] = 0.0342$, wR_2 (all data) = 0.0907.

Acknowledgement

We thank EN-FIST Centre of Excellence, Trg OF 13, 1000 Ljubljana, Slovenia for using SuperNova diffractometer and Slovenian Research Agency (Grant P1-0175).

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New strategies to improve productivity - rMMS microseeding for crystallization and DLS for cryoEM

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Random Microseed Matrix-Screening (rMMS), where seed crystals are added automatically to random crystallization screens, is a significant recent breakthrough in protein crystallization [1]. During the ten years since the method was published, understanding of the theoretical advantages of the method has increased [2 - 4], and several important practical variations on thebasic method have emerged. Important variations that will be discussed include combining seeds from several hits [5], the best methods of selecting hits to optimize [2], and cross-seeding targets with crystals of homologous proteins [6]. We will also present an approach that allows the method to be applied to the crystallization of membrane proteins in LCP [7], and a novel approach to preparing samples for cryoEM using “in situ” dynamic light scattering [8]. This will include discussion of the composition of the ideal screen for cryoEM [9].

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Supramolecular architectures of copper(II) halide complexes with amine and lactame derivatives of pyrazine and pyrimidine

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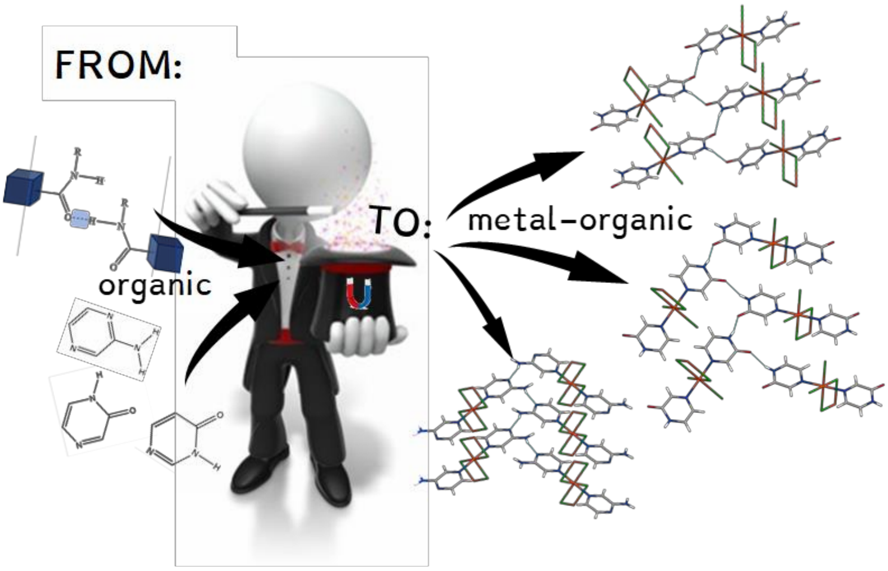
Despite of many robust and reliable supramolecular synthetic strategies that were developed for the organic solid-state systems,[1] targeting specific topologies remains one of the main challenges that the crystal engineering community deals with. That is especially true for the metal-organic systems which have so far received much less attention than their organic counterparts. Those metal-organic systems readily display (at least) two-acceptor systems where the acceptor sites form the organic functionality and the charge-balancing entity compete for the same hydrogen/halogen bond donors. And those rivalries make the assembly process in the metal-organic setting far less predictable.[2-3] Having this in the mind, we opted to explore potential transferability of already established supramolecular strategies from purely organic to metal-organic systems, and at a later step to derive some structure-property relationships.

For that purpose, we prepared a series of copper(II) halide coordination polymers with pyrazine and pyrimidone derivatives equipped with the amine and lactame functionalities. We have found that the involvement of halide anions as charge-compensating entities did not disrupt the intended supramolecular motifs as these remained the same as in purely organic systems. In addition to that, we have also correlated structural observation with magnetic properties.



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Impact of cadmium and phosphate ions on the hematite nanorings formation

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It has been suggested that the addition of divalent metal cations during the hydrothermal synthesis of hematite (α-Fe_2O_3) in the presence of phosphate ions has a strong impact on the hematite morphology, crystal growth and dissolution (Gotić et al., J. Mol. Struct. 993 (2011) 167). In this work, the same system was modified with divalent cadmium ions and the impacts of cadmium and phosphate ions on the hematite nanorings formation have been studied. It has been found that formed hematite and akaganeite (β-FeOOH) precipitates did not contain any trace of cadmium impurities. On the contrary, the modification with divalent cadmium cations changes the PO_4^{3-}/ Fe^{3+} molar ratio in the system. Upon the addition of cadmium ions the PO_4^{3-}/ Fe^{3+} molar ratio changes from 0.036 in a pure system to 0.051 in the cadmium modified system. The relative increase of phosphate concentration at early stage of precipitation induced the change of spindle to spherical morphology and formation of the poorly crystallised akaganeite-like phase. The appearance of akaganeite-like phase directly correlated with the delay in the crystallisation of hematite. Besides, the relative increase of phosphate concentration has the prevailing effect for the change of spindle to pseudosphere and nanotube to nanoring particle morphologies.

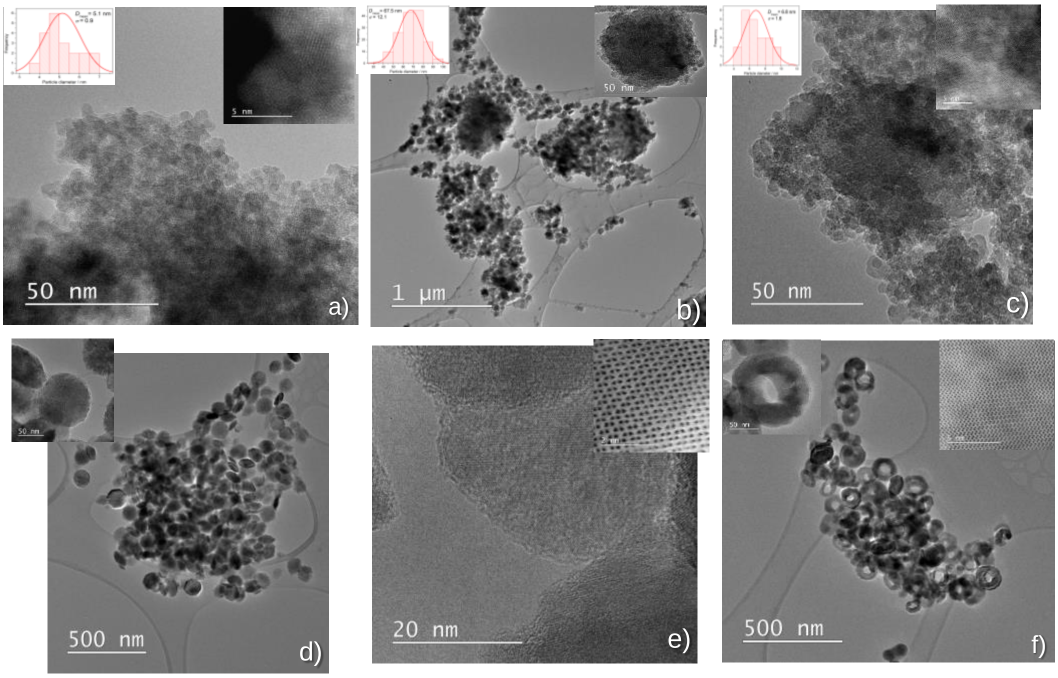

Figure 1: HRTEM images of synthesized samples.

One-pot mechanochemical synthesis of a metal-based halogen-bonded cocrystal with the $CoCl_2L_2$ building block

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Synthesis of metal-based halogen-bonded cocrystals by design remains a poorly developed area of crystal engineering, and is targeted by a number of groups [1]. Following our previous study where we described halogen bonding proclivity of the chlorine atom coordinated to the Co(II) centre [2], herein we describe the use of mechanochemistry, an increasingly popular methodology in rapid and solvent-free synthesis of molecules and materials, for synthesis of a complex metal-organic material by one-pot assembly of metal-ligand bonds and cocrystallisation by halogen bonding [3]. We obtained our metal-organic cocrystal by grinding a mixture of 2-benzoylpyridine (**bzpy**), $CuCl_2(H_2O)_2$ and 1,3,5-triiodotrifluorobenzene (**135tfib**) (Figure 1). To facilitate characterization of the new cocrystal by single-crystal X-ray diffraction, mechanochemical experiments were accompanied by crystallization. Single crystals were grown using the liquid-liquid diffusion method due to very low solubility of the Cu(II) complex. In the crystal structure of the obtained material each $CuCl_2$(**bzpy**)$_2$ unit is connected with **135tfib** *via* I···Cl halogen bonds (d(I2···Cl1) = 3.210 Å, ∠(C–I···Cl) = 173.4°) leading to the formation of supramolecular chains. The chains are connected into a 3-D network by means of C-H···Cl and C–H···O contacts. Molecular structure of the $CuCl_2$(**bzpy**)$_2$ unit is in good agreement with that of the reported *trans*- isomer of the pure complex [4]. The Cu(II) atom is coordinated by two N and two O atoms from two **bzpy** molecule and two Cl atoms, forming a structure with octahedral geometry.

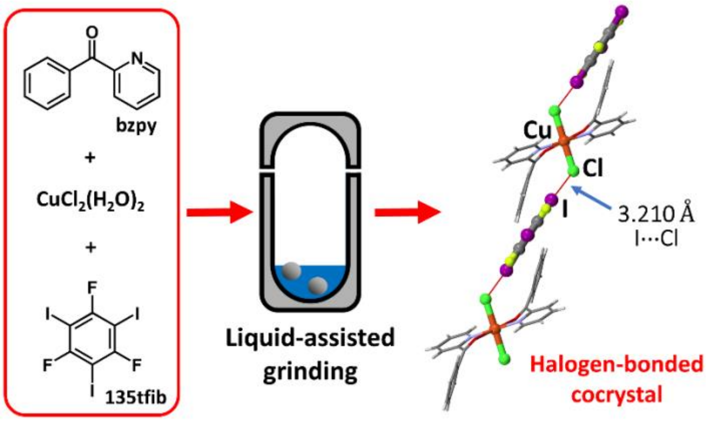

Figure 1: Mechanochemical synthesis of a halogen-bonded metal-organic cocrystal: diagrams of reactants, and fragment of the crystal structure in the resulting cocrystal.

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The study of pyridine adducts of $VO(acac)_2$ in the solid state and solution

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Adduct formation between oxovanadium(IV) diketonates and Lewis bases has been well examined.[1-4] The Lewis bases coordinate in the sixth coordination site of the vanadium atom either in *trans*- or *cis*- position with respect to the vanadyl oxygen. The position in which the Lewis base is coordinated depends on the basicity and steric effect of the Lewis base.[5]

In this study we have examined the formation of adducts between bis(pentane-2,4-dionato)oxovanadium(IV) (**$VO(acac)_2$**) and a set of pyridine derivatives.

Amongst eight adducts whose crystal structures were determined, it was detected that pyridine, 3-methylpyridine and 4-methylpyridine formed *trans*− adducts with **$VO(acac)_2$**, whereas 4-benzoylpyridine and 4-acethylpyridine formed a *cis*− adducts. 2-Amino-3-methylpyridine and 2-amino-5-methylpyridine formed N-H···O hydrogen bonds between the amino group of the pyridine and oxygen atoms of the chelate ring of the complex. In case of 2,4,6-trimethylpiridine and 2-amino-6-methylpyridine, adducts did not form with pyridine nitrogen, but rather a water molecule coordinated on **$VO(acac)_2$** which in turn formed two O-H···N hydrogen bonds with two pyridine molecules. Similarly, when 4-pyridone (4-hydroxypyridine) was used water molecule coordinated on **$VO(acac)_2$** forming O-H···O hydrogen bonds with oxygen atom of 4-pyridone molecules, while NH groups of pyridone formed bifurcated N-H···O hydrogen bond with vanadyl oxygen atom.

The formation of the adducts was also studied in solution. The stability constants of the adducts in MeCN were determined *via* spectrophotometric titrations and were correlated with corresponding Hammet substituent coefficients and pK_a values of the pyridine derivatives. The stereochemistry (*cis or trans*) of the obtained complexes (in the solid state) has been to depend on the basicity of the Lewis base and it is reflected in the characteristic UV-spectra of the adduct.

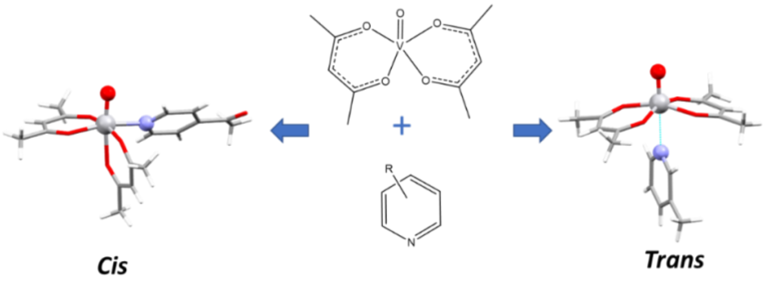

Figure 1: Formation of cis and trans adduct.

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Supramolecular diversity in copper(II) complexes with L-homoserine/L-serine and heterocyclic bases

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Copper(II) complexes with heterocyclic bases and amino acids have been in focus of research in the past several decades due to their versatile properties. These type of complexes are already used in anticancer therapy as they show pronounced antiproliferative activity [1,2]. Moreover, copper(II) complexes with amino acids are capable of forming a vast variety of supramolecular motifs [3], which make them interesting compounds not only in crystal engineering, but also in catalysis, molecular recognition, and investigation of metal-protein interactions. In our recent research we have focused on the investigation of (amino acidato)copper(II) complexes and manipulation of their crystal structures in the solid state [2].

In this research we report two new structures of copper(II) complexes with the L-homoserinate ion (hser) and either 1,10-phenantroline (phen) or 2,2'-bipyridine (bpy): $[\mathrm{Cu}(\mu\text{-hser})(\mathrm{H_2O})(\mathrm{bpy})]_2\mathrm{SO_4}\cdot 4\mathrm{H_2O}$ (**1**) and $[\mathrm{Cu}(\mu\text{-hser})(\mathrm{H_2O})(\mathrm{bpy})][\mathrm{Cu}(\mu\text{-hser})(\mathrm{bpy})]\mathrm{SO_4}\cdot 6\mathrm{H_2O}$ (**2**). Interestingly, no crystal structures of homoserine complexes have been deposited in the Cambridge Structural Database so far [3]. Both complexes crystallize as 1D coordination polymers interconnected by π-interactions and hydrogen bonds, producing 3D supramolecular frameworks. **1** crystallizes in the monoclinic space group $P\ 2_1$, while **2** crystallizes in the triclinic space group $P\ 1$. A comparative study of copper(II) complexes with L-serine/L-homoserine and 2,2'-bipyridine/1,10-phenantroline will be presented, including the structural characteristics and chemical properties. It was shown that subtle changes in synthetic or atmospheric conditions can make a significant difference in the crystal packing.

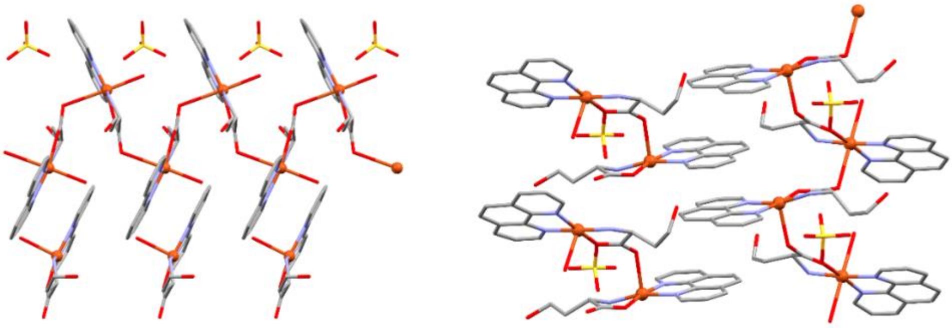

Figure 1: Packing in the crystal structure of complex **1** (left) and **2** (right). Hydrogen atoms and watermolecules are omitted for clarity.

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Influence of the intramolecular hydrogen bonding on structures and stability of adducts of copper and zinc β-diketonates with *N*-donor ligands

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Transition metal β-diketonates are very well investigated coordination compounds which are often used as building blocks in crystal engineering.[1,2] Metal(II) diketonates may exist either as the discrete complexes in square-planar or tetrahedral geometry, oligomers, or as adducts formed by binding of one or two neutral molecules to the metal center. Depending on how many additional molecules are bonded to the metal diketonate, square-piramidal or octahedral geometry of the complex could arise. If a ligand of interest contains a functional group able to act as hydrogen bond donor, then intramolecular hydrogen bonding can be established which could affect overall stability of the complex as well as crystal packing.

In order to study the effects of intramolecular hydrogen bonding on stability of such compounds, several adducts of bis(diketonato)zinc(II) and copper(II) (wherein diketonate ligands were acetylacetone – **acac**, dibenzoylmethane – **dbm**, dipivaloylmethane – **dpm** and acetyl-benzoylmethane – **abm**) were prepared by crystallization from three different solvents (pyridine – **py**, morpholine – **morph** and 2-amino-3-methylpyridine – **2a3mp**). Crystallization experiments yielded eight adducts of **2a3mp**, where intramolecular $\mathrm{N_{amino}}$–H···$\mathrm{O_{diketo}}$ hydrogen bond have been observed. This interaction was also found in **morph** adducts whose formation have been observed exclusively for copper(II) complexes. Furthermore, pyridine adducts have been obtained only with bis(diketonato)zinc(II) compounds and there, as was expected, no intramolecular hydrogen bonding was found. Decomposition of the prepared compounds were analysed by thermogravimetry and differential scanning calorimetry, confirming the general trend of complexes with additional hydrogen bonds being more stable.

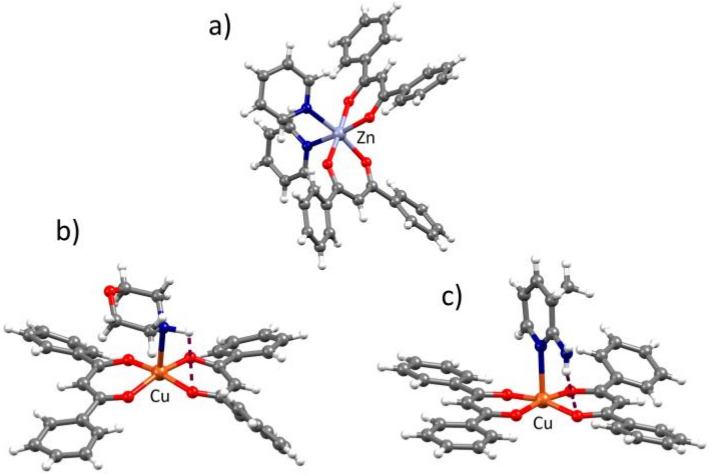

Figure 1: Molecular structures of the a) [Zn(**dbm**)$_2$(**py**)$_2$]; b)[Cu(**dbm**)$_2$(**morph**)] and c) [Cu(**dbm**)$_2$(**2a3mp**)]. Only in the adducts with **morph** and **2a3mp** intramolecular HB have been found.

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X-Ray Identification and Characterization of Azobenzene Palladacycles Obtained by Solid-State C–H Bond Activation

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Cyclopalladated complexes or palladacycles are successfully applied in many areas of material science and biological chemistry. Their preparation is usually performed in solution but number of reports on the solid-state synthesis of these organometallic complexes is steadily growing. Recently, our group reported a successful solid-state synthesis of azobenzene palladacycles in a ball mill that was followed by a detailed mechanistic study of C–H bond activation in azobenzene by various palladium (Pd) precursors, *i.e.* polymeric $PdCl_2$, monomeric $[PdCl_2(MeCN)_2]$, trimeric $[Pd(OAc)_2]_3$ and ionic $[Pd(MeCN)_4][BF_4]_2$.

Herein we report on X-ray diffraction identification and characterization of palladacycles obtained by C–H bond activation in 4-chloro-4’-(*N,N*-dimethylamino)azobenzene by various Pd(II) precursors in a ball mill (Figure 1). Each type of the employed Pd(II) precursor afforded a structurally different mono- and/or dipalladated complex. Structural analysis shows that all monopalladated products have a palladated *p*-(*N,N*-dimethylamino)phenyl ring, which agrees with a regioselective solid-state reaction. Reactions with acetate and chloride Pd(II) precursors afford dimeric and monomeric dicyclopalladated complexes, respectively. Obtained results show a strong influence of the ancillary ligands on the molecular structure of the analyzed palladacycles and support the proposed mechanistic scheme for double palladation of azobenzenes in a ball mill by different Pd(II) precursors.

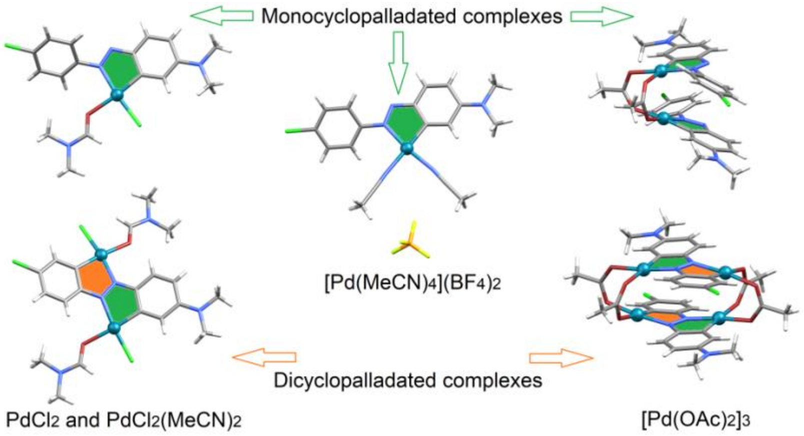

Figure 1: Structurally characterized palladacycles obtained by single or double solid-state C–H bond activation in 4-chloro-4’-(*N,N*-dimethylamino)azobenzene by various Pd(II) precursors.

Structural characterization of 3D coordination polymers of copper(II) and short, uncharged side chain amino-acids with a 4,4’-bipyridine linker

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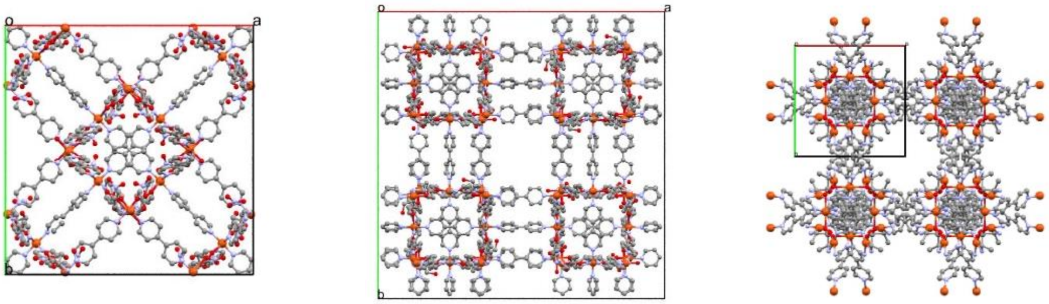
In the recent decades, synthesis and structural characterization of 3D coordination polymers (**cp**) has become a research area of great interest, primary because of their reversible storage and separation potential. They are typically composed of several secondary building units (**SBU**) interconnected by linker molecules, while more than one topology can be constructed using the same **SBU** [1]. The use of bioavailable materials such as amino-acids (**AA**) presents an easy way of introducing chirality into 3D **cp**. It also provides an opportunity of studying the **AA** side chain effects on the conformation of coordination compounds without restraints related to close packing in crystal structures.

Three different types of 3D **cp** of copper(II) with an **AA** (L-serine, L-homoserine, L-threonine, L-alanine, L- and D-valine) and 4,4’-bipyridine (**bpy**) as a linker, were obtained by solution synthesis. Depending on the **AA** type and the crystallization temperature different structural isomers can be obtained. In all compounds, two types of nodes can be clearly distinguished. The first type is trigonal and consists of a Cu(II) ion coordinated with a deprotonated **AA** and two **bpy** molecules. The second type is a tetragonal node made of a Cu(II) ion bound to four **bpy** molecules. Both node types share a common **bpy** linker. The trigonal and square nodes are further arranged in different types of **SBU** with various node ratios. These **SBU** are then interconnected by carboxylate groups. The topologies of the resulting metal-organic frameworks are substantially different. In the first type **SBU** form helices connected by **bpy** linkers, while in the second and in the third they form paddlewheel-like structures. In all compounds the solvent containing voids comprise up to 60 % of unit cell volume. L-serine yielded all three types of **cp**, L-threonine yielded topologies **b)** and **c)** (Figure 1), L-homoserine **b)** while L-alanine, L- and D-valine yielded only topology **c)** (all are shown in Figure 1).



a) **b)** **c)**

Figure 1. Packing diagrams showing three different types of prepared coordination polymers.

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Acknowledgement

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Chloride- and oxalate-bridged heterometallic [$Cu^{II}Cr^{III}$] compounds with 2,2′:6′,2″-terpyridine – the influence of the starting copper(II) salt

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Enormous efforts are made in synthesizing of new homo- and heterometallic coordination polymers of 1D, 2D, and 3D structures. Incorporation of both organic and inorganic components in these compounds has created a new dimension in searching for functional materials that have desired structures and properties. In the design of heteropolynuclear complexes an important role belongs to the oxalate ion, C_2O^{2-}, because of its various possibilities of coordination to metal centers as well as its ability to mediate magnetic interactions between paramagnetic metal centres. Stable mononuclear anionic oxalate complexes such as tris(oxalato)metalate anions, $[M^{III}(C_2O_4)_3]^{3-}$ (M^{III} = Mn, Cr, Fe, V), are often used as ligands toward another metal ion for the preparation of extended multifunctional systems. In addition, the introduction of organic ligands containing *N*-donors, into the metal–oxalate systems prevents the formation of highly insoluble oxalate species and, moreover, influences the nuclearity and topology of the metal centres and stabilizes their solid-state structures.

Applying the layering technique, the deep green prismatic crystals of compound $[Cu_4(\mu\text{-}Cl)_3Cl_2(terpy)_4][Cr(C_2O_4)_3]\cdot 9H_2O$ (**1**) grew from the reaction of an aqueous solution of $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$ and methanol solution containing $CuCl_2\cdot 2H_2O$ and tridentate ligand 2,2′:6′,2″-terpyridine (terpy). Interestingly, the crystal structure of **1** (space group *P*1) consists of the chloride- bridged tetranuclear cation of copper(II), $[Cu_4(\mu\text{-}Cl)_3Cl_2(terpy)_4]^{3+}$, the mononuclear $[Cr(C_2O_4)_3]^{3-}$ anion and nine molecules of water of crystallization.

Using the same technique, solvents and reactants, but using $Cu(NO_3)_2\cdot 3H_2O$ instead of chloride salt, green prismatic crystals of complex salt $[Cu(H_2O)_3(terpy)][Cu(H_2O)(terpy)(\mu\text{-}C_2O_4)Cr(C_2O_4)_2]_2\cdot 7H_2O$ (**2**), crystallizing in $P2_1/c$ space group, are formed. The structure **2** contains one symmetrical mononuclear $[Cu(H_2O)_3(terpy)]^{2+}$ cation, two symmetry-equivalent oxalate-bridged heterodinuclear $[Cu(H_2O)(terpy)(\mu\text{-}C_2O_4)Cr(C_2O_4)_2]^-$ anions and seven water molecules of crystallization. In addition to the single crystal X-ray diffraction study, characterization of the new complexes has been accomplished by means of the IR spectroscopy and thermal analysis.

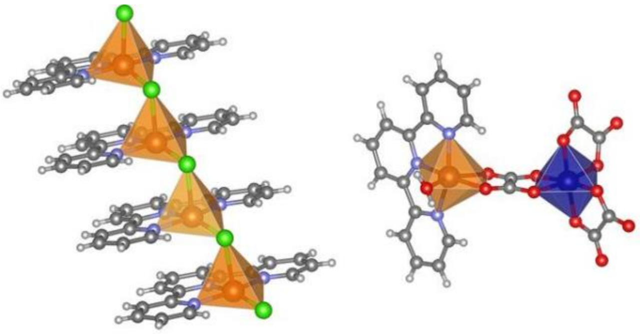
(a) (b)

Figure 1. VESTA drawing of (a) the chloride-bridged tetranuclear [Cu4(*μ*-Cl)3Cl2(terpy)4]$^{3+}$ cation in compound **1** and (b) the oxalate-bridged heterodinuclear [Cu(H2O)(terpy)(μ-C2O4)Cr(C2O4)2]$^-$ anion in compound **2**, showing coordination polyhedra around metal centres. The Cu and Cr atoms are depicted in orange and blue colours, respectively.

Understanding the role of weak interactions in responsivness of molecular crystals to external mechanical stimuli

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Crystal engineering, since its very beginning some twenty years ago, has always been accompanied by profound interest in deeper understanding of intermolecular interactions and their subsequent use in deliberate formation of solid-state structures.[1] Nowadays, it has reached such a point where we can successfully synthesize many of desired supramolecular connectivities and topologies, and grow crystalline solids of desired morphologies. These crystalline materials have for a long been believed to be brittle and inelastic, and that upon application of even relatively insignificant mechanical stress they readily crack and/or break. Recently, we have been witnessing a growing number of literature reports on mechanically responsive molecular crystals.[2,3] They can flex elastically or plastically once external mechanical force is applied, and in all the examples, macroscopic behavior is likely a consequence of substantial anisotropy of intermolecular interactions. We have also recently observed flexible response to applied mechanical force for a class of acicular crystals of cadmium(II) coordination polymers,[4] and results clearly demonstrated a need for deeper understanding of the explicit connection between form and function.

In this contribution, we report on a similar class of coordination polymers of cadmium(II) with pyrazine-based ligands bearing functionalities capable of forming desired supramolecular links that allow us correlation of slight structural changes and mechanical response. The crystals have also shown substantial elastic response to applied external stimuli.

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Dioxovanadium(V) complexes with 2-benzothiazolyhidrazones as potential antitumor agents

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Combining biologically active benzothiazole, hydrazone and quinoline structural fragments in a unique molecular system results in 2-benzothiazolylhydrazone ligands with increased coordination capabilities and enhanced antitumor activity [1,2]. Antitumor properties of vanadium compounds are primarily investigated on vanadocenes, oxovanadium(IV) and dioxovanadium(V) complexes [3]. Appropriate ligand systems can improve stability and transport of complex compounds as well as synergistically enhance pharmacological activity through combination of several modes of antitumor activity.

The reaction of [VO(acac)$_2$] with H$_2$L$^{1-5}$/HL^{6,7} (H$_2$L$^{1-5}$=Bzt–NH–N=CH–RXY, R$^{1-4}$=C$_6$H$_3$, R^5=C$_{10}$H$_6$, X=2–OH, Y^1=H, Y^2=3-OH, Y^3=4-OH, Y^4=5-OH, Y^5=H; HL^{6,7}=Bzt–NH–N=CH–R, R^6=C$_5$H$_4$N, R^7=C$_9$H$_6$N) in alcohol solutions in a stoichiometric ratio of 1:1 resulted in seven complexes of general formula [VO$_2$HL$^{1-5}$]/[VO$_2$L^{6,7}]. Reaction of [VO(acac)$_2$], H$_2$L$^{1-5}$ and triethylamine in a stoichiometric ratio of 1:1:1 resulted in five Et$_3$NH[VO$_2$L$^{1-5}$] complexes.

The proposed structural formulae of compounds were proved by spectroscopic methods (FT-IR, ^{1}H and ^{13}C NMR), elemental and thermogravimetric analysis. The crystal and molecular structures of six dioxovanadium(V) complexes ([VO$_2$HL^{1,5}], [VO$_2$L^6] and Et$_3$NH[VO$_2$L^{1,3,5}]) were determined by the single crystal X-ray diffraction method. In complex compounds vanadyl moiety is coordinated in a distorted square pyramidal environment with monoanionic *ONO*/*ONN* tridentate ligands in neutral complexes and with dianionic *ONO* ligands in ionic complexes (Figure 1).

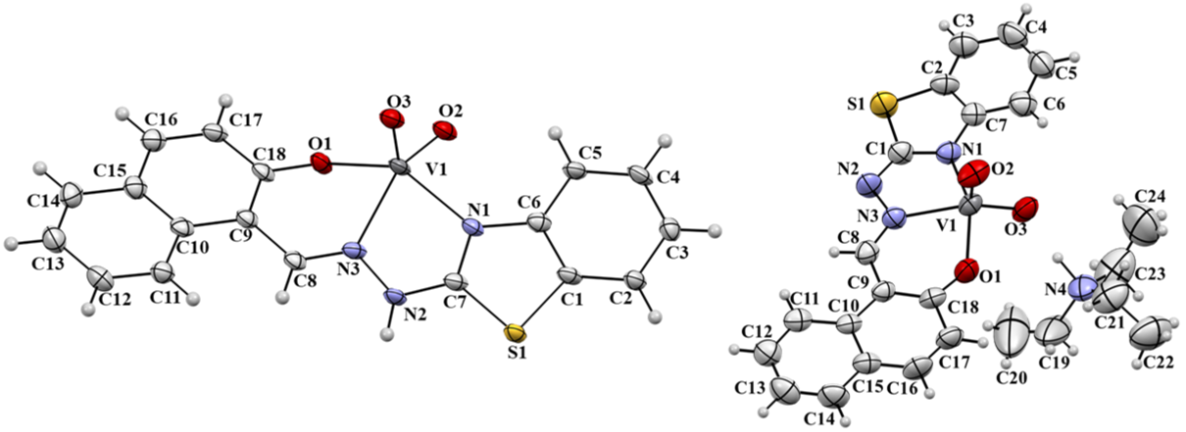

Figure 1: Molecular structures of [VO$_2$HL^5] (left) and Et$_3$NH[VO$_2$L^5] (right)

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Upgrading Home-Lab X-ray Diffractometers with Incoatec´s Unique Microfocus Source

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Modern microfocus X-ray sources define the state-of-the-art for a broad spectrum of applications in home laboratories, such as protein and small molecule crystallography, and small-angle scattering. These sources are combined with multilayer Montel optics to image the source spot onto the sample. These Montel optics provide a 2D parallel or 2D focused monochromatic X-ray beam, magnified to a suitable size.

Low power sealed microfocus sources, such as Incoatec’s IµS represent an attractive alternative to rotating anodes, with a significant reduction in cost and maintenance. Power loads of a few kW/mm2 in anode spot sizes below 50 micrometer deliver a compact and very brilliant beam. For example, the new IµS 3.0 delivers more than $2.4*10^{10}$ photons/s/mm^2 in a focal spot size of below 100 micrometer diameter at the sample position, and, therefore, comes close to the performance of modern microfocus rotating anodes. It is available for Cu, Mo, Ag, Cr and Co anodes. Since the launch in 2006 about 850 IµS systems are now in operation worldwide for a large variety of applications in biology, chemistry, physics and material science.

Are you tired of getting spare parts for an ancient rotating anode or is your detector performance only limited by your x-ray source that lacks intensity?

We will demonstrate how to bring former high end diffractometers back to a superb performance for cutting edge science after an upgrade with a high performance IµS source. Incoatec ensures full software and safety integration, and an installation hand in hand with your local service responsible, providing a constant service support by your partners on site.

In addition to all Bruker and Nonius systems, Incoatec also offers integrations into a wide range of instruments, e.g. Rigaku, marXperts, STOE, also together with Dectris or Huber components. We also provide customized special engineering solutions.

Figure 1: Typical upgrade projects, where an IµS replaced an old X-ray source (sealed tube or rotating anode) or was added within a customized setup.

Crystal chemistry of metal-rich R–T–C carbides

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Ternary R–T–C (R = rare earth, T = *d*-element) carbides are classified into two groups: metal-rich carbides or intermetallics and carbometalates containing polyanions $[T_yC_z]^{n-}$ ranging from discrete units to clusters, chains, layers, and 3D networks [1]. The bonding in these two classes of carbides is different. Metal-metal interactions prevail over all other ones in the group of intermetallic carbides while in carbometalates these interactions are also present but not dominant. Compositions of metal-rich carbides are localized in the T-rich corner of concentration triangle. They are characterized with the ratio $4 \leq M/C \leq 16$ (M = R and T). These compounds are perspective for developing of new functional materials. They are stable in air and display metal-like properties.

Ni-rich ternary carbides are of particular interest due to the electronic structure of this element, which has in normal state 10 electrons on upper level ($3d^84s^2$ or $3d^94s^1$). That's why M-rich R–Ni–C structure types are inherent to Ni-containing compounds only among other 3*d*-element containing carbides. Among eight structure types of R–T–C intermetallics known to date we will focus on the following three structure types occurring for T = Ni ternary compounds: $Yb_{11}Ni_{60}C_6$ (structure type I) with $M:C \approx 12$; $Ce_2Ni_{22}C_{3-x}$ (str. type II) with $M:C \approx 9$; and $Er_4Ni_{13}C_4$ (str. type III) with $M:C = 4.25$. Their crystal structures are characterized by high coordination number for metal atoms. Two species of carbon atoms occur in the structures: isolated C atoms (str. types I–III) and C_2-units (str. type III). Coordination polyhedra of carbon species in these structures are shown in Figure. Details on synthesis, stability, structural relations and magnetic properties of already known as well as of recently obtained by authors R–Ni–C carbides will be presented.

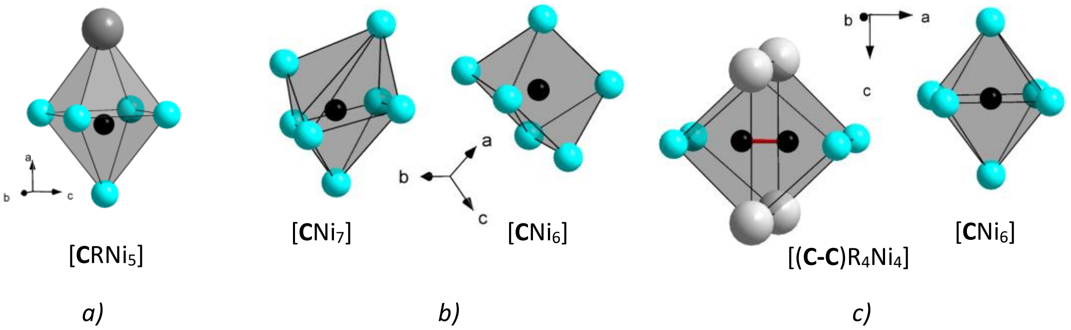

Figure: Coordination polyhedra of carbon atoms in the crystal structures of $Yb_{11}Ni_{60}C_6$ *(a)*, $Ce_2Ni_{22}C_{3-x}$ *(b)*, and $Er_4Ni_{13}C_4$ *(c)* prototypes

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Incommensurately modulated crystal structures of $[XeF_5][As_xSb_{1-x}F_6]$ (x ~0.3 and ~0.5)

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Crystallization of dissolved in anhydrous hydrogen fluoride $[XeF_5][AsF_6]$ and $[XeF_5][SbF_6]$ mixtures in various starting ratios resulted in the single crystals of $[XeF_5][As_{0.3}Sb_{0.7}F_6]$ and $[XeF_5][As_{0.5}Sb_{0.5}F_6]$. The $[XeF_5][As_{0.5}Sb_{0.5}F_6]$ crystallizes in two crystal modifications at low (α-phase, T < 180 K) and high (β-phase, T > 180 K) temperatures. α-$[XeF_5][As_{0.5}Sb_{0.5}F_6]$ is orthorhombic with *Pca2₁* space group, a=9.9738(2) Å, b=13.2492(4) Å, c=23.3701(7) Å, V= 3088.24(14) Å^3 at 150 K, Z=8. The (3+1)-dimensional modulated structure of β-$[XeF_5][As_{0.5}Sb_{0.5}F_6]$ belongs to the orthorhombic superspace group Ama2(00g)s0s with a=10.1196(5) Å, b=13.4517(6) Å, c=11.8999(5) Å, V=1619.8(2) Å^3 at 296 K, Z=4. The same incommensurately modulated structure was determined for $[XeF_5][As_{0.3}Sb_{0.7}F_6]$ in the temperature range of 150…296 K. Both 3-d and (3+1)-d structures consist of discrete XeF_5^+ cations and AF_6^- ($A=As_xSb_{1-x}$) anions. All metalloids positions are mixed occupied by As and Sb atoms with higher As amount for one position and *vice versa* for the other one.

Structural Investigations of Organic Geminal Dihydroperoxides

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Organic peroxides possessing a reactive O−O linkage are an interesting class of compounds with diverse applications. They appear as initiators of radical reactions, bleaching agents, energetic materials, and also as important intermediates in organic syntheses. Furthermore, organic peroxo compounds exhibit a broad-spectrum of bioactivity. The most famous example being the endoperoxide antimalarial drug artemisinin [1].

Geminal dihydroperoxides are possible precursors for the synthesis of medicinally interesting 1,2,4,5-tetraoxanes [2] and have also been investigated as candidates for primary explosives [3]. However, extensive structural studies of these species are hampered by their sensitivity and the often hazardous nature of their crystalline forms. The aforementioned stability issues can be circumvented by cocrystallization with hydrogen-bond acceptors [4].

A recent synthetic procedure for selective peroxidation of ketones with aqueous hydrogen peroxide activated by azeotropic removal of water [5] enabled the crystallization of neat geminal dihydroperoxides and their characterization by low-temperature single-crystal X-ray diffraction. In addition to pure phases, crystal hydrates or perhydrates of certain *gem*-dihydroperoxides were obtained. Studied crystal structures display intricate patterns of O−H···O hydrogen bonds and offer insights into the hydrogen-bonding donor/acceptor preferences of the HOO− group.

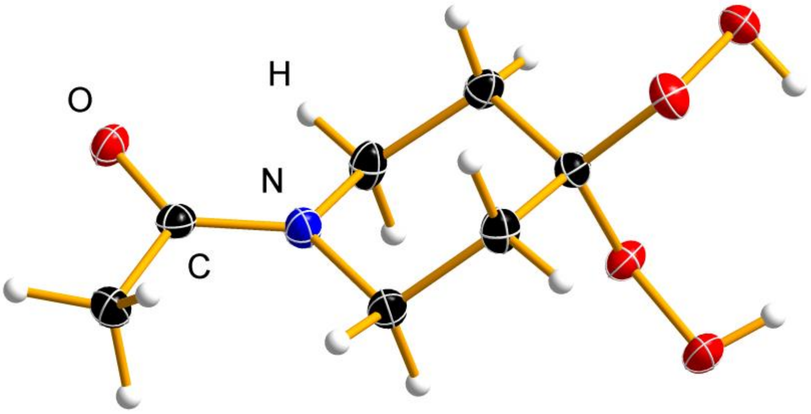

Figure: The asymmetric unit of the geminal dihydroperoxide derivative (thermal ellipsoids are depicted at the 50% probability level and hydrogen atoms as spheres of arbitrary radius).

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Preparation of the Ba_2CrNbO_6 and $NiNb_2O_6$ Oxides by Thermal Decomposition of the Mixture of Oxalate Precursors

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Beside their applications in catalysis, photoluminescence, magnetism, gas storage and separation, metal-organic coordination systems have recently been used as molecular precursors for the preparation of the mixed metal oxides by their thermal decomposition. It has been observed that the use of a well-defined heterometallic precursor can produce crystalline oxide materials under conditions that are significantly milder than those applied in traditional solid-state synthesis. Moreover, the single-source precursors provide better control over the stoichiometry of the metal ions in the final products as well as the homogeneity of the materials due to the mixing of the metals at the molecular level. The existence of bridging or chelating ligands in the precursors prevents metal separation during oxide formation. The $C_2O_4^{2-}$ anion easily decomposes to the vapour phases CO_2 and CO, by the low-temperature routes, and hence, heterometallic oxalate complexes are very convenient for the preparation of mixed metal oxides [1].

Heterometallic oxalate complexes do not always contain the appropriate stoichiometry for the formation of the desired single phase mixed-metal oxide. So, we have tested whether the multimetallic oxides could be prepared by mixing two or more different oxalate precursor in various ratios prior to thermal decomposition [2].

A highly crystalline materials Ba_2CrNbO_6 were obtained after thermal decomposition of the mixture of the well-defined and structurally characterized oxalate-based compounds $\{Ba_2(H_2O)_5[NbO(C_2O_4)_3]HC_2O_4\}\cdot H_2O$ [3] and $(NH_4)_3[Cr(C_2O_4)_3]\cdot 3H_2O$ taken in equimolar ratio and grinded in agate mortar prior to heating treatment. Following the same strategy, oxide $NiNb_2O_6$ was prepared from the mixture of $[Ni(bpy)_3]_2[NbO(C_2O_4)_3]Cl\cdot 12H_2O$ [4] and $(NH_4)_3[NbO(C_2O_4)_3]\cdot H_2O$ [3] complexes, taken in a 1: 3 ratio.

The phase formation and structural ordering of oxides obtained by modified *molecular precursor-to-material* method has been investigated through a combination of thermal analysis (TGA and DTA) and powder X-ray diffraction.

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Crystallographic study of cadmium(II) complexes with 2-acetylpyridine-aminoguanidine and bromide as coligand

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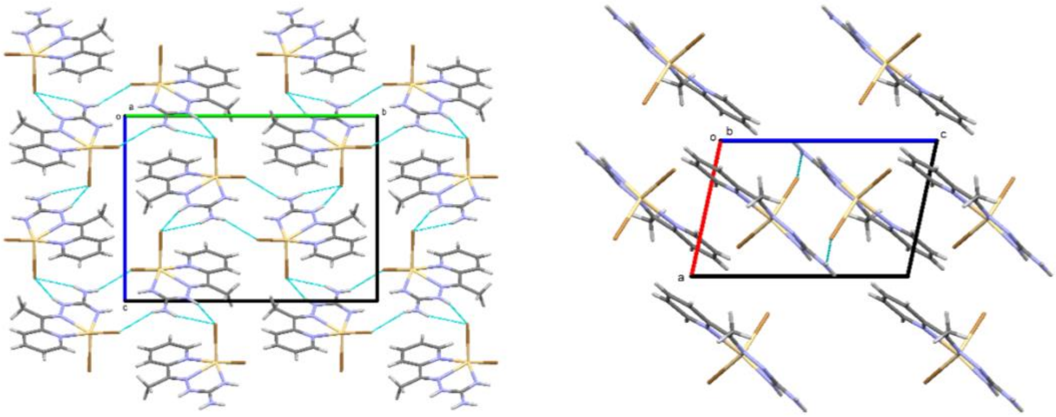
The interest in syntheses of 2-acetylpyridine Schiff bases and their metal complexes arose due to their considerable in vitro activity against some human tumor lines [1, 2]. On the other hand, Schiff bases of aminoguanidine and their metal complexes have wide range of biological activities, but this group of compounds is also very important in organic synthesis as well as in catalysis. Since group 12 metal complexes usually show high photoluminescence and have potential applications as optoelectronic devices [3], it would be interesting to explore the influence of coordination on all of the mentioned properties of the described Schiff bases.

The reaction of warm water solutions of 2-acetylpyridine-aminoguanidine hydrogen chloride (L·2HCl) and cadmium(II)-bromide resulted in formation of pale yellow single crystals of the complex [Cd(L)Br$_2$] (**1**). The polymorph **2** was obtained by recrystallization of complex **1** from methanol. In both complexes chelating ligand is coordinated in its neutral form in a usual tridentate N$_3$ manner, through pyridine and azomethine nitrogen atoms and nitrogen atom of aminoguanidine moiety. The polymorph **1** crystallizes in monoclinic crystal system in *P*2$_1$/n space group, while the polymorph **2** crystalizes in triclinic crystal system in *P*-1 space group. Cadmium(II) is situated in a distorted square-pyramidal geometry with τ parameter 0.12 for **1** and 0.16 for **2**.



(a) (b)

Figure 1: Crystal packing of polymorph **1** projected on *bc* plane (a) and polymorph **2** projected on *ac* plane (b).

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Ag/TiO$_2$ nanoparticle composites and their photocatalytic performance

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In this work we present simple chemical method for preparation of Ag/TiO$_2$ nanoparticle composites and investigate their photocatalytic performance under visible and UV-enriched irradiation sources. The coupling of metallic additives with TiO$_2$ (anatase, rutile or mixed phase tetragonal structures), results in extension of the absorption range, higher utilization of the visible light, and might lead to the faster photocatalytic degradation of pollutants, due to more efficient charge separation. Proposed method involves usage of chitosan, a bio-derived polysaccharide rarely utilized in ceramics-related research, which serves as both stabilizing and reducing agent. We present thorough characterization of the structural, textural and optical properties, performed on the obtained powders by the means of FE-SEM, TEM, XRD, SAED, BET and UV-VIS-NIR spectroscopy. Microscopical analysis revealed the reduction of TiO$_2$ particles size, upon the introduction of silver into the system, and presence of sub-10 nm TiO$_2$ particles decorated with sub-3 nm Ag dots in the composite samples (0-15wt% of Ag). Structural analysis disclosed pure or predominant presence of anatase crystallographic phase. Higher surface area compared to commercial referent samples was obtained. Also, the enhancement of visible light absorption was detected in the composite samples, compared to pure TiO$_2$. The photocatalytic degradation of textile azo dye (Reactive Orange 16) and antibiotic (Nutrofurantoin) was investigated, showing very high adsorption capability of the powders, and superior photocatalytic behaviour compared to referent samples.

Tetrahedrally-coordinated boron in Fe-bearing dravite from a metamorphic schist from Brandrücken, Weinebene, Koralpe, Styria, Austria

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The highest boron content (ca. 0.8 apfu ${}^{[4]}B$) in a natural tourmaline was observed in an Al-rich sample from the Stoffhütte, Koralpe, Austria [1]. A greenish tourmaline (from a different locality at the Koralpe), found in 2003 in a metamorphic rock (mica schist or paragneiss), not far from the Brandrücken exploration adit (Weinebene lithium deposit), was structurally characterized by single crystal X-ray diffraction ($R1$ = 1.81%). This tourmaline with lattice parameters a = 15.930(1), c = 7.196(1) Å, has shown that the X site (<X-O> = 2.674(1) Å) is occupied by Na and some Ca. The <Y-O> distance with 2.021(1) Å is not very large, compared to very Mg-rich samples. The <Z-O> distance with 1.926(1) Å is enlarged, compared to samples containing only Al at the smaller [6]-coordinated Z site. By releasing the Z-site occupancy in a preliminary refinement with only Al at this site, the refined occupancy was smaller than for a Z site fully occupied with Al. Hence, it is very likely that also ca. 0.90 *apfu* Mg occupy this site. The <Y-O> distance with 2.021(1) Å shows together with the results of the refinement, that the Y site is most likely occupied mainly by Mg, Al and some Fe^{2+}. The O1 position (W site) contains in addition to (OH,O) a significant amount of fluorine. Interestingly the <T-O> distance with 1.618(1) Å is slightly reduced, compared to a T site, which is only occupied by Si. Together with the refinement results, there is evidence for a small amount of boron at the T site. A similar tourmaline, a metamorphic Fe-bearing dravite, which was significantly more enriched in Fe, was described by [2] from a glaucophane schist from Syros, Greece, associated with omphacite. That sample experienced slightly larger lattice parameters (a = 15.944, c = 7.209 Å) and its formation (at PT conditions of ca. 6 to 7 kbar/ ca. 400°C) took place in a subduction-exhumation environment.

Based on the structure refinement the tourmaline from Brandrücken exhibits the approx. formula ${}^{X}(Na_{0.90}Ca_{0.10})$ ${}^{Y}(Mg_{1.50}Al_{1.34}Fe^{2+}_{0.16})$ ${}^{Z}(Al_{5.10}Mg_{0.90})$ $(BO_3)_3$ ${}^{T}[Si_{5.90}B_{0.10(2)}O_{18}]$ ${}^{V}(OH)_3$ ${}^{W}[(OH,O)_{0.8}F_{0.2}]$. Tetrahedrally-coordinated boron has been observed very rarely in Mg-rich tourmaline to date. Although this sample was found in a mica schist or paragneiss, it is not clear, if it was formed during the eo-alpine metamorphic high-pressure event or already during the permian-triassic crustal extension, where the spodumen-bearing pegmatites (one of the largest Li deposits worldwide) at Weinebene took place. Although lithium was not analyzed, we do not expect a significant amount in this Mg-rich tourmaline sample, because it was not originated in a pegmatitic rock. However, the small, but significant amount of boron at the tetrahedral position seems to be well established.

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A new copper(II) arsenate, $Na_2Cu_3(AsO_3OH)_4 \cdot 4H_2O$ containing discrete $[Cu_3O_{12}]^{18-}$ units: synthesis, crystal structure and magnetic properties

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Single crystals of the new disodium tricopper(II) tetrakis(hydrogenarsenate(V)) tetrahydrate, $Na_2Cu_3(AsO_3OH)_4 \cdot 4H_2O$ were grown under hydrothermal conditions. The compound was characterized by room-temperature single-crystal X-ray diffraction, SEM-EDS analysis, Raman spectroscopy and magnetic susceptibility measurements.

$Na_2Cu_3(AsO_3OH)_4 \cdot 4H_2O$ represents a new layered structure-type [space group $P2_1/c$, $a = 8.7089(17)$, $b = 9.7452(19)$, $c = 9.3353(19)$ Å, $\beta = 92.63(3)$ °, $V = 791.4(3)$ Å^3, $Z = 4$]. The layers are normal to [100] and are composed of the isolated Cu_3O_{12} units interconnected by AsO_3OH coordination tetrahedra (Fig. 1). The crystal structure of $Na_2Cu_3(AsO_3OH)_4 \cdot 4H_2O$ is related to a group of compounds formed by Cu^{2+}–$(XO_4)^{3-}$ layers ($X = P^{5+}$, As^{5+}) linked by M cations (M = alkali, alkaline earth, Pb^{2+}, or Ag^+) and partly by hydrogen bonds [1], where distinct links and patterns of the Cu_3O_{12} units and XO_4 tetrahedra were observed.

The magnetic susceptibility and magnetization measurements reveal a canted antiferromagnetic ground state (Fig. 1) which is in excellent agreement with a layered magnetic structure determined by the copper ions of the Cu_3O_{12} units.

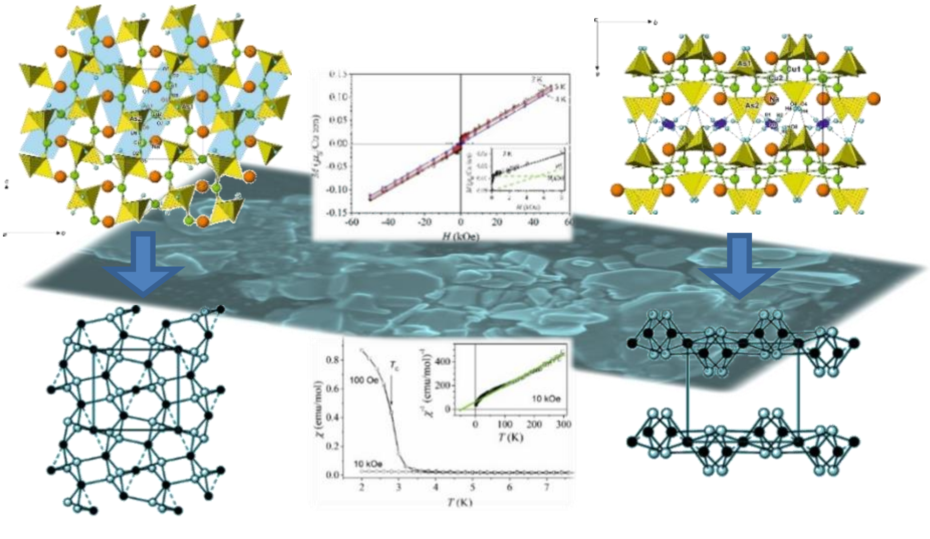

Figure 1: Crystal structure of $Na_2Cu_3(AsO_3OH)_4 \cdot 4H_2O$ and its nodal representation with black nodes drawn for CuO_x (x = 4, 5, 6) polyhedra and white for AsO_4 tetrahedra. Magnetization curves and temperature dependent susceptibility are also pictured.

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$BiFeO_3$-based nanoparticles obtained by different synthetic routes and their structural, optical and photocatalytic properties

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The preparation of pure $BiFeO_3$ (BFO) powders and ceramics is still a challenging issue because of a narrow temperature range of phase stabilization. The mechanism of BFO synthesis reaction usually includes formation of secondary phases. In this work, BFO precursor powders were synthesized by hydro-evaporation (HE) and ultrasound (US) assisted sol–gel method. BFO precursor powder obtained by HE method was calcined at various temperatures ranging from 620°C to 770°C for 6 h; while powder obtained by US route was thermally treated at 500°C for 30 min, to form resulting BFO powders. Structural, optical, and photocatalytic properties of the obtained powders were investigated. The X-ray diffraction analysis of BFO powders prepared by HE method, confirmed the presence of secondary phases, $Bi_{25}FeO_{39}$ and $Bi_2Fe_4O_9$. On the other hand, X-ray diffraction analysis confirmed the formation of pure phase nanosized BFO obtained by US route. Therefore, BFO powder obtained by US method was selected for photocatalytic degradation of typical organic azo dye Mordant Blue 9 in concentration of 50 mg/l. The determined band gap of US obtained BFO powder was 2.20 eV, indicating its potential application as visible-light-response photocatalyst. Measurements were performed for different times of irradiation and *p*H of the dye solution. Photodegradation products were analysed by HPLC technique, and mechanism of photocatalytic degradation of organic dye was proposed.

Halogen-bonded complexes of perhalogenated hydrocarbons and benzoyl-4-pyridoylmethane

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Halogen bond is an attractive interaction between an electrophilic region on a halogen atom in a molecular entity (halogen bond donor) and a nucleophilic region in another, or the same, molecular entity (halogen bond acceptor).[1] Alongside hydrogen bond, it is a widely used tool for constructing supramolecular assemblies in the solid state, where perhalogenated hydrocarbons have been highlighted as the most important halogen bond donors.[2] On the other hand, potential of using β-diketones for the synthesis of a halogen-bonded structures in the solid state has scarcely been investigated to date, indicated by only 6 structures deposited with the CSD.[3]

In this contribution we are presenting crystal structures of a novel asymmetric β–diketone, benzoyl-4-pyridoylmethane (**b4pm**) and cocrystals derived from **b4pm** and five usual halogen bond donors: iodopentaflourobenzene (**ipfb**), 1,2-, 1,3- and 1,4-diiodotetraflorobenzene (**1,2-tfib**, **1,3-tfib** and **1,4-tfib**) and 1,3,5-triiodo-2,4,6-trifluorobenzene (**1,3,5-titfb**). These binary solids have been prepared both by crystallization from solution and liquid-assisted grinding (LAG). All five cocrystals are assembeled by C—I···N halogen bonds involving pyridyl nitrogen and iodoperfluorobenzene iodine. Furthermore, cocrystals derived from **1,3-tfib** or **1,2-tfib** have additional C—I···O halogen bonds, involving oxygen atoms from β-diketo group and the other iodine atom. Most of the obtained cocrystals contain one **b4pm** molecule connected to a corresponding halogen bond donor, except for **(b4pm)$_2$(1,4-tfib)**, where stoichiometry is 2:1 as a result of **1,4-tfib** bridging two diketone molecules via C—I···N halogen bonds. All obtained compounds have been characterized by X-ray powder diffraction, thermogravimetry and differential scanning calorimetry.

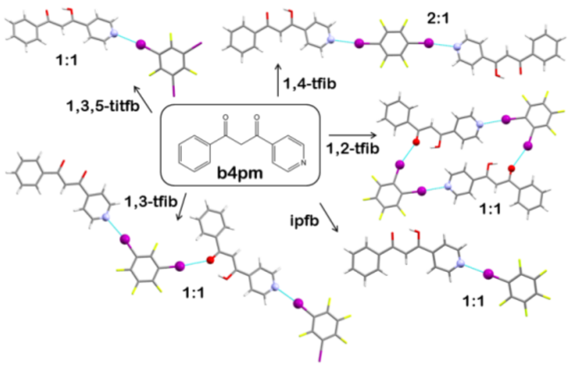

Figure 1: Halogen-bonded complexes of perhalogenated hydrocarbons and benzoyl-4-pyridoylmethane

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Proof-of-concept: flexible receptor in complexes with malonic acid

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Synthetic anion receptors can differ in the rigidity of their molecular structure that can reflect on the peak-selectivity level of binding the target species [1]. While they usually show poorer selectivity compared to their rigid counterparts, flexible receptors can adopt their conformation or self-assemble in complex supramolecular species in order to respond to the anion demands and achieve chemical complementarity [2-5].

Herein we report the study of self-assembly process of flexible polyamine receptor and malonic acid in methanol and ethanol. Single crystal X-ray studies revealed two new structures, which confirm that the length of the spacer unit (in acid molecule) as well as the aromatic nature of anion play crucial role in recognition and binding. To test our hypothesis, competitive milling experiments showed that recognition and binding can be performed in the solid state with the selectivity trend: maleic > malonic > succinic ≈ fumaric acid which is explained by the influences of both the relative orientation of carboxylic groups and partial aromaticity of explored anions.

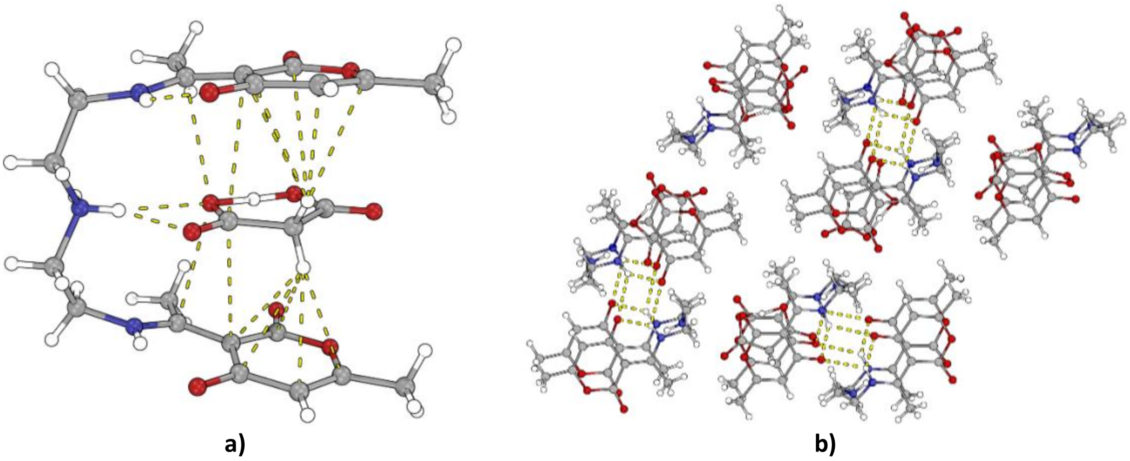

Figure 1: **a)** Molecular structure of the receptor-acid complex. **b)** Crystal packing viewed down crystallographic *b* axis. An array of yellow cylinders represents either H-bonds or close contacts.

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Cooperativity of halogen bonds in cocrystals of 4-halogenoanilines and 1,4-diiodotetrafluorobenzene

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One of the most notable features of halogen bonding [1] is that it involves halogen atoms that are electrophilic species, but that can also be nucleophilic due to induced electron density anisotropy [2]. When considering interactions between two halogen species, it is necessary to differentiate between two types: type I, which arise from close packing requirements, and type II, which represent the interaction between the nucleophilic area of one halogen and the electrophilic area of another halogen and are therefore considered halogen bonding motifs [3]. Our goal in this work was to explore the possibilities in halogen bonding involving halogenated anilines, seeing as halogen atoms and ligands are known halogen bond acceptors [1,3] and as their amine functional group is also a potential halogen bond acceptor [4].

We selected structurally equivalent reactants, 4-chloroaniline (**4ClA**), 4-bromoaniline (**4BrA**) and 4-iodoaniline (**4IA**), so as to study the effects on the supramolecular interactions on crystal packing. First, we performed mechanochemical and solution based synthesis, reacting each 4-halogenoaniline with 1,4-diiodotetrafluorobenzene (**14tfib**) in a 2:1 molar ratio. Products were characterized by means of powder X-ray diffraction and by single crystal X-ray diffraction. The three obtained products are isostructural. In all three cases **14tfib** forms remarkably similar halogen bonds only with the amine group (d(I···N) = 3.000 - 2.996 Å, ∠(C–I···N) = 178 – 177 °), leaving the halogen atom of the 4-halogenoanilines to participate as both a halogen bond donor and acceptor in a type II contact. The geometry of the observed type II contacts is shown to be only slightly dependent on the donor capabilities of the halogen atom (d(I···I) = 3.892 Å, ∠(C–I···I) = 169 °; d(Br···Br) = 3.666 Å, ∠(C–Br···Br) = 165 °; d(Cl···Cl) = 3.623 Å, ∠(C–Cl···Cl) = 165 °). The combination of halogen bonding and type II contacts leads to the formation of layers which are then further stacked into 3D.

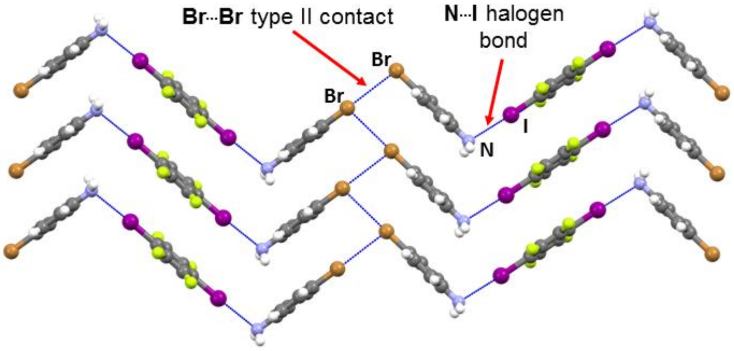

Figure 1: Fragment of the crystal structure in (**4BrA**)(**14tfib**).

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Halogen bonded cocrystals of *N*-bromophthalimide with 2-chloro- and 2-bromopyridine

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N-Haloimides are commercially available compounds, commonly used for halogenation in organic synthesis. Since they possess an extremely polarized halogen atom, they represent a new group of potent halogen bond (XB) donors that form very strong and close-to-linear halogen bonds with N- and O-containing acceptors *via* the robust $(CO)_2N–X\cdots N$ halogen bond synthon (X = Br, I) [1-3]. As a member of this group, *N*-bromophthalimide (**nbph**) has shown significant potential as a halogen bond donor for preparation of binary molecular solids with nitrogen bases [4].

In this work we present the cocrystallization of *N*-bromophthalimide (**nbph**) by both mechanochemical synthesis and the conventional solution-based method. As cocrystal coformers, we have selected 2-chloropyridine (**2ClPy**) and 2-bromopyridine (**2BrPy**). From a crystal engineering standpoint, the coformers are interesting due to the presence of a pyridine nitrogen atom as a potential strong halogen bond acceptor and an additional halogen atom (Br or Cl) as a potential acceptor and donor of another halogen bond. Obtained cocrystals were isostructural, with the dominant supramolecular interaction being the halogen bond between the *N*-bromophthalimide bromine and the pyridine nitrogen, while the halogen of the pyridine ring participated only in substantially longer halogen-halogen (type I) contacts.

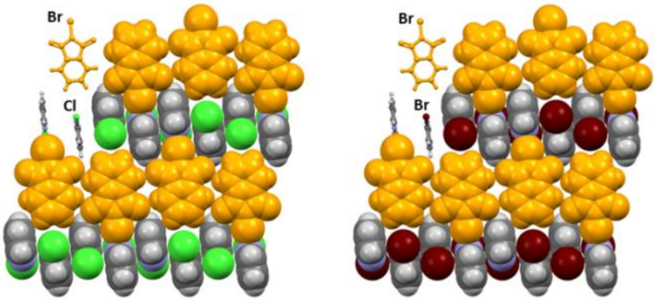

Figure 1: Crystal structures of (**2ClPy**)(**nbph**) and (**2BrPy**)(**nbph**) cocrystals.

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Indo-Italian Macromolecular Crystallography (MX) Beamline XRD2 at Elettra Synchrotron Light Source

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Macromolecular Crystallography (MX) is a technique used by Structural Biology researchers to determine the structures of biological macromolecules such as nucleic acids and proteins to atomic resolution. The macromolecular structures help to elucidate the detailed functional mechanism in living cells and organisms. A new MX beamline XRD2 at Elettra synchrotron facilitates the data collection on the protein crystals with large tunable energy range (*8.0 - 35.0keV*) suitable for SAD/MAD experiments. The beamline is built and commissioned in collaboration with Indian MX community. Currently, the beamline is under pilot phase of operation and within the next beamtime period the operations will be ramped up and will start providing the beamtime to international community. The beamline is under continuous development to adopt the state-of-the art best tools for the MX experiments. Currently, the beamline is equipped with Pilatus 6M detector, Microdiffractometer (MD2S) and new flex family sample changer compatible with spine sample holder. Beamline overview, description and capabilities will be presented together with initial results from the high quality data collected at the new beamline.

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Poreč, Croatia

Hotel Diamant
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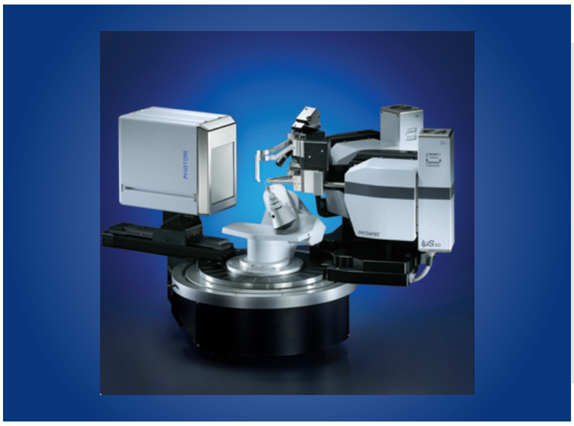

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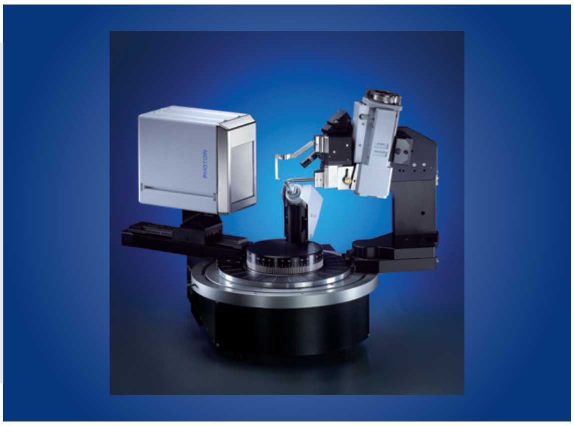

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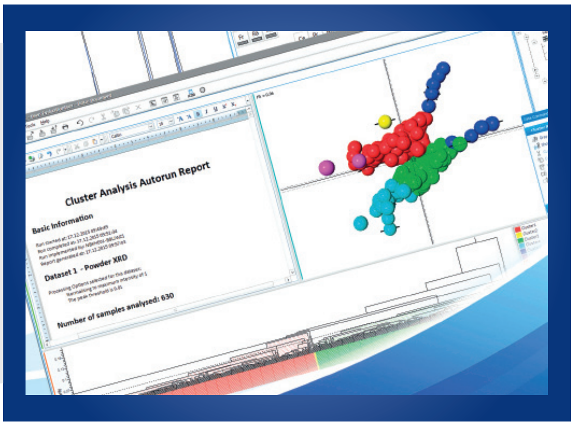

Cluster Analysis Autorun Report

Basic Information

Dataset 1 - Powder XRD

Number of samples analysed: 630

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Croatian-Slovenian and Slovenian-Croatian Crystallographic Meetings

1st SCCM - 1992, ***Otočec***, Slovenia, on the banks of the beautiful and clear Krka river, flowing close to an old medieval burgh

2nd CSCM - 1993, ***Stubičke Toplice***, Croatia, in the picturesque and green Croatian Zagorje

3rd SCCM - 1994, ***Kranjska Gora***, Slovenia, at the foot of the sky scraping Julian Alps

4th CSCM - 1995, ***Trakošćan***, Croatia, again in the Croatian Zagorje, near a romantic medieval castle, now a museum of fine arts

5th SCCM - 1996, ***Zreče***, Slovenia, at the foot of the monumental Pohorje Mountain

6th CSCM - 1997, ***Umag***, Croatia, on the west Istrian, Adriatic, coast

7th SCCM - 1998, ***Radenci Spa***, Slovenia, in a green picturesque north-east and wine-rich part of Slovenia

8th CSCM - 1999, the ***Red Island***, Croatia, off-shore of the town of ***Rovinj,*** the ***west*** Istrian coast, enjoying a splendid isolation from civilization

9th SCCM - 2000, ***Gozd Martuljek***, Slovenia, close to the very heart of the Julian Alps

10th CSCM - 2001, ***Lovran***, Croatia, on the east Istrian coast, near Opatija and at the foot of the powerful Učka Mountain

11th SCCM - 2002, ***Bohinj***, (Hotel *Jezero*) Slovenia, in the heart of the famous Triglav National Park

12th CSCM - 2003, ***National Park Plitvice Lakes*** (Hotel *Jezero*), Croatia, UNESCO protected natural world heritage

13th SCCM - 2004, ***Bovec***, Slovenia, at the bank of the unique Soča river, flowing among the Alps

14th CSCM - 2005, ***Vrsar***, Croatia, halfway between Poreč and Rovinj, the famous tourist resorts in Istria

15th SCCM - 2006, ***Jezersko***, Slovenia, an important climatic resort, between two mountain ranges, Karavanke and Kamnik-Savinja Alps

16th CSCM - 2007, ***Petrčane***, Croatia, between Zadar and Nin, famous historic places, full of antique Roman and middle age Croatian monuments

17th SCCM - 2008, ***Ptuj***, Slovenia, the oldest town in Slovenia, the sister town of Varaždin

18th CSCM - 2009, ***Varaždin***, Croatia, a baroque town and a former Croatian capital

19th SCCM - 2010, ***Strunjan***, Slovenia, a tourist resort on the west Istrian coast, famous for the salt works

20th CSCM - 2011, ***Baška***, Croatia, a famous tourist resort on the island of Krk, the place where the oldest monument of the Croatian language was found

21st SCCM - 2012, ***Pokljuka***, Slovenia, in the middle of Julian Alps, isolated from civilization at 1300 m above the sea level

22nd CSCM - 2013, ***Biograd***, Croatia, a famous tourist resort in the middle of the Croatian Adriatic coast, once the crown town of Croatian kings

23rd SCCM - 2014, ***Logar Valley***, Slovenia, one of the most picturesque Slovenian valleys, surrounded by Julian Alps

24th CSCM - 2016, ***Bol***, the island of Brač, Croatia, a famous tourist resort in the middle of the Croatian Adriatic

25th SCCM – 2017, ***Ljubljana***, Slovenia, a capital and largest city, known for its green spaces

26th CSCM – 2018, ***Poreč***, a beatuful touristic city on the western coast of the Istrian peninsula, whose history dates 6000 years back

Croatian-Slovenian Crystallographic Meetings in IUCr newsletters:

CRYSTALLOGRAPHIC MEETING REPORTS

Summer of crystallography in Croatia

Bol, Croatia, September 2016
http://cscm24.xyz

BY MARIO CETINA, STANKO POPOVIĆ AND ANTON MEDEN

The 24th Croatian-Slovenian Crystallographic Meeting (CSCM24) was held in September of 2016 at Bol on the island of Brač in the Adriatic Sea. Together with the 3rd European Crystallographic School that followed, it was a great summer of crystallography in Croatia.

The meeting was jointly organized by the Croatian Crystallographic Association (CCA) and the Slovenian Crystallographic Society (SCS), under the auspices of the Croatian Academy of Sciences and Arts. The Chair of the Organizing Committee was Mario Cetina (CCA). The Chairs of the Meeting were Stanko Popović (CCA) and Anton Meden (SCS). Overall, 98 scientists participated in the meeting coming from Croatia (59), Slovenia (12), Austria, Germany, Italy, Korea, Poland, Serbia, South Africa, Switzerland and the UK.

Five plenary and eighty short oral contributions were presented. The plenary lectures included: "Handling crystal pathologies in macromolecular crystallography" (M. Jaskolski, Poland); "Flexibility, Dynamics and Chemical Reactions in Solids: Molecular Crystals to Framework Materials" (L. Brammer, UK); "Direct imaging and quantification of crystal structures at the atomic level using C_s corrected scanning transmission electron microscope" (G. Dražić, Slovenia); "Crystallography and Society: outcomes of IYCr2014" (M. Zema, UK);"Thermosalient crystals- acrobatics on the nanoscale" (Ž. Skoko, Croatia).

Short oral contributions dealt with modern development of crystallography and closely related fields and gave students an excellent opportunity to gain experience presenting to a large scientific audience.

As there was no registration fee for this meeting, the Organizing Committee is thankful for financial support of the sponsors: PANalytical I Renacon (The Netherlands I Croatia), Rigaku (UK), Bruker I Aparatura (Germany, Austria, Croatia), Douglas Instruments (UK), Stoe (Germany), Dectris (Switzerland), PLIVA Croatia Ltd., Croatian National Tourist Board, Bluesun Hotels (Croatia). All information about the meeting can be found at http://cscm24.xyz.

An excursion to Pučišća included visits to a stone carving school, a wine cellar, and Vidova Gora Peak, the highest peak on the island.


The Vidova Gora Peak, view on Bol and neighbouring islands.


Plenary lecturers (l to r): Ž. Skoko, M. Jaskolski, G. Dražić, L. Brammer and M. Zema in the wine cellar in Bol.


Participants in the Klesarska škola (Stone-carving School), Pučišća.

Comments from the plenary lecturers

M. Jaskolski: *The Island of Brač and Bol have left unforgettable impressions and memories.*

L. Brammer: *I am impressed with the very nice work being done in Croatia, The meeting format provides excellent opportunities for students to get experience in giving presentations to a larger scientific audience. The meeting certainly had the familiar, welcoming feeling that I find is present at most crystallographic meetings.*

G. Dražić: *I learned many new things and surely I will attend the future meetings.*

M. Zema: I enjoyed the atmosphere, the presence of so many young and promising crystallographers and all discussions and conversations. Not to mention the beautiful scenery of Croatia and Bol in particular!

The 25th SCCM will be held in Ljubljana, Slovenia , June 15–17, 2017, http://slocro25.fkkt.uni-lj.si/

Report to IUCr Newsletter

25th Slovenian-Croatian Crystallographic Meeting
Ljubljana, Slovenia, June 2017

By ANTON MEDEN, DUBRAVKA MATKOVIĆ ČALOGOVIĆ, STANKO POPOVIĆ

The 25th Slovenian-Croatian Crystallographic Meeting was held in June 2017 in the city of Ljubljana in the newly built Faculty of Chemistry and Chemical Technology. There were 79 registered participants from Austria, Germany, India, Russian Federation, South Africa, United Kingdom, Croatia and Slovenia. Five plenary lectures were presented: "High-pressure studies of organic and coordination compounds" (Prof. Elena Boldyreva, Novosibirsk, Russia), »More than 100 years of Lewis' diagrams – still valid in the light of charge density?" (Prof. Dietmar Stalke, Göttingen, Germany), "Powder Diffraction: an Essential Complementary Tool for those Skilled in the Art but one with Pitfalls for the Unwary" (Dr. Jeremy Karl Cockcroft, London, UK), "Stacking of planar conjugated rings – beyond aromatics" (Dr Krešimir Molčanov, Zagreb, Croatia) and "Microstructure evolution in cermet anodes for solid oxide fuel cells" (Prof. Marjan Marinšek, Ljubljana, Slovenia). To enrich the program of the Meeting, Olex2 workshop was also organized (Dr. Horst Puschmann, OlexSys & Durham University, UK).

One of Slovenian-Croatian Meetings' advantages is that all participants give an oral presentation, which gives young scientists the opportunity to present their work in a friendly but in professional atmosphere. Fifty-nine short oral presentations addressed contemporary topics in crystallography: structure determination of organic, inorganic and coordination compounds, crystal architecture and design, phase transitions, solid solutions, structure-properties relationship, synergy of diffraction and complementary techniques, and history.

The Meeting was organized jointly by the Faculty of Chemistry and Chemical Technology, University of Ljubljana, and the Croatian Crystallographic Association under the auspices of Univ. of Ljubljana and promoted by Slovenian Chemical Society. There was no registration fee. Therefore we thank the sponsors, donors and advertisers: European Crystallographic Association, Renacon, Rigaku, Bruker, MiTeGen, Crystal Impact, Stoe, Dectris, Mettler Toledo, Aparatura, Lek-Sandoz, Laboratorij-um and Scan.

More information about the Meeting can be found on http://slocro25.fkkt.uni-lj.si/.

Plenary lecturers (from the left): H. Puschmann, J.K. Cockcroft, E. Boldyreva, D. Stalke, K. Molčanov, missing M. Marinšek.

Poreč, Croatia, the venue of the Meeting

The 26th Croatian-Slovenian Crystallographic Meeting will be held from 13th to 17th of June 2018. in a beautiful Adriatic city Poreč, Croatia, located in the western coast of Istrian Peninsula. Poreč is located less than 60 km from Pula which is the main airport in the region. From the airport, there are public shuttle buses that operate to Poreč. Also, there are frequent busses from Zagreb, as well as passenger ferries from Venice, Italy. Poreč is situated on the West coast of the largest Croatian peninsula, Istria whose smaller parts spread into Slovenia and Italy. This town's history goes 6.000 years back and it preserved its urban nucleus from the period it was a Roman colony Parentium. The names of its principal streets are still called Decumanus and Cardo as in Roman times. Through its long history Romans, Byzantines, Venetians, and Napoleon ruled Poreč. It was a part of Austro-Hungarian Monarchy, Italy and Yugoslavia. The old town is a protected monument on a tiny peninsula once guarded by fortification walls and towers. From the facades of its buildings one can learn about history of architecture, but most valuable building is Early Christian complex Eufrasiana from the 6 th century. From 1997 it is a part of UNESCO's World Heritage. The town spreads outside its walls in such a manner that Mediterranean landscape has been preserved. Actual Poreč is known for its protected environment, its oak and evergreen forests, vineyards and olive groves spreading almost to the seashore. Tourism began developing in 19 th century after opening the first public beach on Island St. Nicolas. The first hotel was constructed in 1910. The sea is clear here and bathing season lasts from May till October. Poreč has 17.000 inhabitants but in summer hosts to 70.000 tourists in hotels, camps and resorts well known for comfortable and active holidays.

CROATIAN CRYSTALLOGRAPHIC ASSOCIATION
FACULTY OF CHEMISTRY AND CHEMICAL TECHNOLOGY,
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THE TWENTY-SIXTH CROATIAN - SLOVENIAN CRYSTALLOGRAPHIC MEETING

Poreč, Croatia
June 13 - 17, 2018

BOOK OF ABSTRACTS AND PROGRAMME

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