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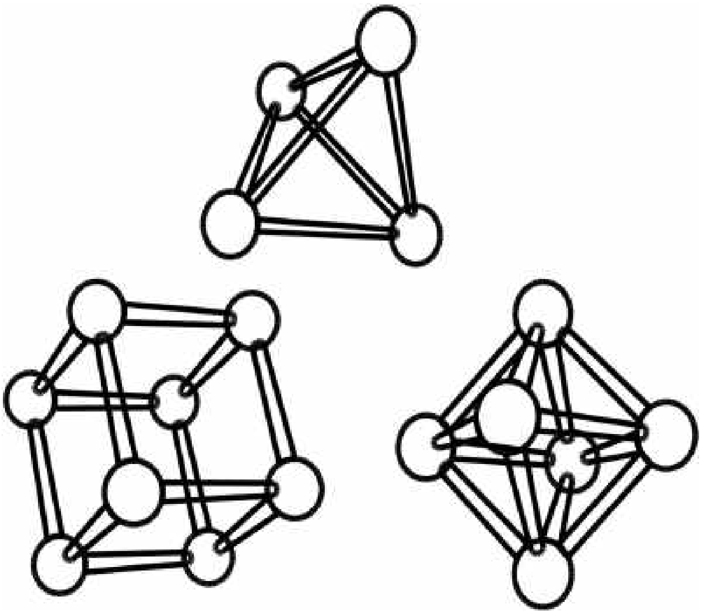
THIRTIETH CROATIAN-SLOVENIAN CRYSTALLOGRAPHIC MEETING



BOOK OF ABSTRACTS

12-16 June, 2024

Veli Lošinj, Croatia

The 30th Croatian-Slovenian Crystallographic Meeting

is organized jointly by the *Croatian Crystallographic Association*, *Faculty of Chemistry and Chemical Technology*, and the University of Ljubljana under the auspices of the Department of Mathematical, Physical, and Chemical Sciences of the *Croatian Academy of Sciences and Arts*.

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PROGRAMME

WEDNESDAY, June 12, 2024

19^{00} – 19^{30} **REGISTRATION OF PARTICIPANTS**
19^{30} **WELCOME RECEPTION**

THURSDAY, June 13, 2024

8^{00} – 8^{45} **REGISTRATION OF PARTICIPANTS**
8^{45} – 9^{00} **OPENING CEREMONY**

Chairpersons: A. Meden, D. Matković-Čalogović

9^{00} – 10^{00} **PLENARY LECTURE**
Ivan Halasz
In situ powder X-ray diffraction and Raman spectroscopy for monitoring of ball-milling mechanochemistry

Chairperson: I. Đilović

10^{00} – 10^{30} COFFEE BREAK

SHORT PRESENTATIONS

Chairpersons: B. Kozlevčar, I. Đilović

10^{30} – 10^{40} **Anton Meden**
X-Ray Powder Diffraction of High-Entropy alloys
10^{40} – 10^{55} **Željko Skoko**, J. Popović, S. Popović
XRD “microscopy”: a case of in-situ formation of the Al–Zn solid solution
10^{55} – 11^{05} **Eugen Libowitzky**
Structure distortion of diamond-polished cuprite surface layers and its impact on Raman spectra
11^{05} – 11^{15} **Ines Kulašić**, N. Petek, J. Svete, U. Grošelj, B. Štefane
Structural determination of novel pyrazolone and diazepine derivatives
11^{15} – 11^{35} T. Strürzer, C. Lenczyk, J. Graf, **Martin Adam**
Bridging the gap between Electron and X-ray Diffraction
11^{45} – 12^{00} BREAK

	SHORT PRESENTATIONS
	Chairpersons: N. Bedeković, P. Stanić
12^{00} – 12^{10}	**Nina Podjed**, Z. Uranjek, B. Modec Zinc(II)-based coordination chemistry of furosemide: from complexes to coordination polymer
12^{10} – 12^{25}	M. A. Pipp, N. Podjed, **Barbara Modec** Zinc(ii) coordination polymer containing quinaldinate and 2-hydroxypyridine ligands
12^{25} – 12^{35}	**Mateja Pisačić**, B. Tokić, M. Đaković Crystals under the spotlight – discovering the possibilities of crystals' dynamic behaviour
12^{35} – 12^{45}	**Uroš Rapuš**, J. Kljun, I. Turel Suprising structure of a rhenium(I) complex
12^{45} – 12^{55}	**Marta Počkaj**, B. Košmrlj Cobalt(III) complex with in situ formed ligand derived from 2-pyridinemethanol
12^{55} – 13^{10}	S. Marijan, T. Klaser, P. Mošner, L. Koudelka, Ž. Skoko, J. Pisk, **Luka Pavić** Investigating the glass-forming region in sodium phosphate-niobate-based glass systems
13^{15} – 15^{00}	LUNCH BREAK
15^{00} – 16^{00}	**PLENARY LECTURE** **Laura Cendron** A structural view of SOS response in bacteria: how it works and how to block it **Chairperson:** I. Kekez
16^{00} – 16^{30}	COFFEE BREAK
	SHORT PRESENTATIONS
	Chairpersons: I. Kekez, M. Počkaj
16^{30} – 16^{45}	**Benoit Colasson** Supramolecular design for biomimetic model complexes: Crystallographic considerations from a non-crystallographer

16^{45} – 16^{55}	**Jerneja Kladnik**, L. Rejc, D. Knez, G. Molina-Aguirre, A. Espargaró, A. Meden, L. Blinc, M. Lozinšek, R. D. Jansen-van Vuuren, M. Rogan, B. A. Martek, J. Mlakar, A. Dremelj, A. Petrič, S. Gobec, R. Sabaté, M. Bresjanac, B. Pinter, J. Košmrlj Fluorescent molecular probes for Alzheimer's diagnosis: Synthesis, crystal structures and biological evaluation
16^{55} – 17^{10}	**Aleksandar Višnjevac**, I. Piantanida, O. Reinaud, B. Colasson Co(II) coordination by capped calix[6]arenes
17^{10} – 17^{25}	**Žan Zakošek**, E. Goreshnik Exploration of the ternary system CuBr – HBr – DABCO
17^{25} – 17^{50}	BREAK

Chairpersons: L. Pavić, J. Jakoš

17^{50} – 18^{00}	**Ana Siljanovska**, M. Virant, K. Molčanov, M. Lozinšek, J. Cerkovnik Hydrogen-bonded cocrystals of triphenylarsine oxide
18^{00} – 18^{15}	**Nikola Bedeković,** A. Magnabosco, V. Stilinović, D. Cinčić Pyridine nitrogen as a bifurcated halogen bond acceptor in cocrystals of 1,2-diiodotetrafluorobenzene and pyridine derivatives: CSD survey, structural and computational study
18^{15} – 18^{35}	**Vladimir Stilinović**, N. Baus Topić, E. Topić, L. Fotović Morphotropism in a series of halogen bonded cocrystals derived from an isomorphous series of *N*-(4-halobenzyl)-3-halopyridinium halogenides
18^{35} – 18^{45}	**Matic Lozinšek** Crystal structure of spicy capsaicin
19^{00} – 20^{30}	**Matthew Lightfoot, Lily Hunnisett** CSD WORKSHOP: unlocking new insights thanks to over a million structures

FRIDAY, June 14, 2024

9^{00} – 10^{00}	**PLENARY LECTURE** **Damjan Pelc** Diffuse scattering and nanoscale correlations in quantum materials

Chairperson: M. Lozinšek

10^{00} – 10^{30}	COFFEE BREAK

SHORT PRESENTATIONS

Chairpersons: M. Pisačić, M. Lozinšek

10^{30} – 10^{50}	**Jakub Wojciechowski (Rigaku)** Improving workflows in CrysAlisPro with intelligent devices and automations
10^{50} – 11^{00}	**Bogdan Kotur**, V. Babizhetskyy, C. Zheng, V. Smetana New ternary gallide $Zr_7Pd_{7-x}Ga_{3+x}$ ($0 \leq x \leq 1.8$)
11^{00} – 11^{10}	**Lia Šibav**, M. Lozinšek, Z. Jagličić, A. Zorko, M. Dragomir Crystal growth, structural and magnetic characterisation of $ErTa_7O_{19}$ and $Er_3Ta_{17}O_{47}$
11^{10} – 11^{20}	**Petra Stanić**, K. Molčanov Quantum crystallographic study of pancake-bonded TCNQ radical anions
11^{20} – 11^{40}	**Krešimir Molčanov**, P. Stanić, L. Molčanov, M. Jurić, F. Meurer, M. Bodensteiner, C. Hennig, M. Virant, M. Lozinšek Two-electron multicentre bonding (pancake bonding): from discrete dimers to extended 2D arrays
11^{50} – 12^{00}	BREAK

Chairpersons: L. Molčanov, J. Jakoš

12^{00} – 12^{20}	**M. Arhangelskis**, Y. Xu, M. L. Chodkiewicz, M. Woińska, D. Trzybiński, I. Brekalo, F. Topić, K. Wożniak Hirshfeld atom refinement for metal-organic frameworks: accurate assignment of hydrogen atom positions and detailed analysis of guest disorder
12^{20} – 12^{40}	**Viktoriia Drushliak**, M. Szafrański High-Pressure and Temperature Studies Open New Insights into Two-Dimensional Perovskite $CsC[(NH_2)_3]PbI_4$
12^{40} – 12^{55}	**Yizhi Xu**, J. Dorrell, J. P. Darby, J. M. Marrett, H. M. Titi, A. J. Morris, T. Friščić, M. Arhangelskis High throughput ab initio crystal structure prediction of metal-organic frameworks with machine learning
12^{55} – 13^{05}	**Lily M. Hunnisett**, J. Nyman, N. Francia, G. Sadiq, I. Sugden, J. Cole A Seventh Blind Test of Crystal Structure Prediction Methods

13^{05} – 13^{15}	**Jure Jakoš**, A. Juvan, M. Pesek, M. Marolt, J. Košmrlj, M. Gazvoda Structure elucidation of organic molecules from experimental spectroscopic data using Schmarnica
13^{15} – 15^{45}	LUNCH BREAK
15^{45} – 19^{30}	**Conference trip** (visit the Museum of Apoxyomenos and Lošinj's Fragrant Garden)

SATURDAY, June 15, 2024

9^{00} – 10^{00}	**PLENARY LECTURE** **Catharine Esterhuysen** The role of intermolecular interactions in chemical processes **Chairperson:** M. Đaković
10^{00} – 10^{30}	COFFEE BREAK
	SHORT PRESENTATIONS **Chairpersons:** M. Đaković, Ž. Skoko
10^{30} – 10^{40}	**Mario Cetina**, A. Meščić, S. Raić-Malić Supramolecular architectures of two N-acyclic uracil derivatives
10^{40} – 10^{55}	**Christopher J. Kingsbury,** I. J. Sugden Aromatics Analyser 2 and a unified approach to aromatic interactions
10^{55} – 11^{05}	**Andreas Ertl** A first attempt to use correlations in tourmaline as a thermometer
11^{05} – 11^{20}	**Dominik Talla**, Ž. Zakošek, G. Giester The single-diffusion gel growth technique: a way of preparing novel metal-organic complexes
11^{20} – 11^{30}	**Žan Zakošek**, D. Talla, G. Giester, M. Počkaj Coordination compounds with indole-2- and indole-3-carboxylates
11^{30} – 10^{45}	**Mirjana M. Radanović**, M. S. Kostić, M. V Rodić, N. D. Radnović, Lj. S. Vojinović-Ješić, F. Perdih Synthesis and structure of Cu(I) complex with Schiff base of aminoguanidine and 2-(diphenylphosphino)benzaldehyde

11^{45} – 12^{00}	BREAK
	Chairpersons: K. Molčanov, G. Giester
12^{00} – 12^{10}	**Andrii Hultiaiev**, E. Goreshnik The new Cu(I)-Cl-polyamine compounds
12^{10} – 12^{20}	**Erik Uran**, K. Radan, M. Virant, M. Dragomir, M. Lozinšek Reactivity of cyanogen towards [XeF]+ cation
12^{20} – 12^{30}	**Miha Virant**, V. Milašinović, K. Radan, M. Lozinšek Coordination of carbamoyl fluoride to fluoridoxenon(1+) cation
12^{30} – 12^{40}	**Viktoriia R. Kukharuk**, V. N. Kokozay, E. A. Goreshnik, S. R. Petrusenko (*E*)-*N*'-((5-(hydroxymethyl)furan-2-yl)methylene) benzohydrazide and its copper(ii) complex: synthesis and crystal structure
12^{40} – 12^{55}	**Evgeny Goreshnik**, S. Petrusenko Diversity of mixed cupro(i)-cyano-thiocyanato anionic polymers
12^{55} – 13^{10}	**Bojan Kozlevčar**, A. Pevec Coordination compounds with 5-sulfosalicylates
13^{15} – 15^{00}	LUNCH BREAK
15^{00} – 16^{00}	**PLENARY LECTURE** **Mirela Dragomir** Synthesis and structure-property relationships of selected quantum materials **Chairperson:** V. Stilinović
16^{00} – 16^{30}	COFFEE BREAK
	Chairpersons: V. Stilinović, U. Rapuš
16^{30} – 16^{40}	**Klemen Motaln**, M. Lozinšek On the synthesis and structure of salts containing the peculiar $[MF_3(XeF_2)_3]^+$ (M = Pd, Pt) cations
16^{40} – 16^{50}	**Olha Sanko**, E. Uran, K. Radan, M. Lozinšek Synthesis and Structural Analysis of Novel XeII−N-bonded Compounds
16^{50} – 17^{00}	**Monika Šoltić,** N. Baran, I. Marić, G. Štefanić, M. Marciuš, G. Dražić, R. Peter, T. Jurkin, M. Ivanda, M. Gotić Synthesis, characterization and gas sensing properties of platinum nanoparticles dispersed on iron oxide support

17^{00} – 17^{15}	**Matjaž Kristl**, B. Dojer, T. M. Podnar, A. Golobič Crystal structures of novel copper coordination compounds with pyridinecarbonitriles
17^{15} – 17^{25}	BREAK
17^{25} – 17^{35}	**Mišel Hozjan**, F. Perdih Zinc complexes with derivatives of picolinic acid
17^{35} – 17^{45}	**Kristian Radan**, L. Clough, S. Parsons, M. Lozinšek Recent advances in coordination chemistry of metal complexes with XeF_2 as a ligand
17^{45} – 18^{00}	**Marijana Đaković**, M. Borovina, M. Pisačić, M. Zausnig, I. Kodrin Structure-property relationship in mechanoflexible crystalline coordination polymers
18^{00} – 18^{30}	**CLOSING REMARKS** **Chairpersons:** A. Meden, D. Matković-Čalogović
20^{00}	**CONFERENCE DINNER**

SUNDAY, June 16, 2024

9^{00}	EVALUATION AND FAREWELL COFFEE

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PLENARY LECTURES

IN SITU POWDER X-RAY DIFFRACTION AND RAMAN SPECTROSCOPY FOR MONITORING OF BALL-MILLING MECHANOCHEMISTRY

Ivan Halasz

Ruđer Bošković Institute, Zagreb, Croatia; *Email:* ihalasz@irb.hr

Monitoring of mechanochemical reactions that occur by mechanical agitation and activation has reached a certain level of maturity where these methods are entering into routine use. Powder X-ray diffraction revealed intricate details of transformations of bulk crystalline species and it still requires a synchrotron source, preferrably a beamline capable of producing high-energy photons.[1] The complementary molecular-level monitoring is provided by Raman spectroscopy and the two techniques can best be employed in tandem to study various milling parameters and reacton conditions on mechanochemical reactions.[3]

Using this methodology, we have initially demonstrated a surprisingly dynamic reaction environment where reactions on the 1 mmol scale can be completed within a couple of minutes, where intermediates are encountered more often then not, and where new phases and new polymorphs can be selectively and controllably prepared. We can now also extract reaction profiles both from PXRD and Raman data to study the influence of liquid additives on reaction mechanisms, to study solid-state catalysis and to understand reaction sequences by mapping the energy landscape of the reacting solids.[3] This talk will provide an overview of experimental and theoretical work in mechanistic understanding of chemical transformations in mechanochemical processing achieved by using methods of in situ monitoring and also by chemical methods of isotope labelling of solids.[4] I will put focus on current drawbacks and discuss gaps that deserve development of new methodology including develoment of laboratory-capable in situ diffraction, in situ pair-distribution analysis, and in situ photomechanochemistry.

References:

[1] Katsenis, A. D. et. al. (2015) *Nat. Commun.* 6, 6662.
[2] Lukin, S., Stolar, T., Tireli, M., Blanco, M. V., Babić, D., Friščić, T., Užarević, K., Halasz, I. (2017) *Chem. Eur. J.* 23, 13941.
[3] Lukin, S., Germann, L., Friščić, T., Halasz, I. (2022) *Acc. Chem. Res.* 55, 1262–1277.
[4] Lukin, S., Tireli, M., Stolar, T., Barišić, D., Blanco, M. V., di Michiel, M., Užarević, K., Halasz, I., (2019) *J. Am. Chem Soc.* 141, 1212.

Acknowledgement

This work was in large part financed by the Croatian Science foundation (Grant No. IP-2020-02-1419). We are grateful to the ESRF - The Eutropean Synchrotron for beamtime.

A STRUCTURAL VIEW OF SOS RESPONSE IN BACTERIA: HOW IT WORKS AND HOW TO BLOCK IT

Laura Cendron[1]

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The SOS response is a crucial bacterial mechanism in response to genotoxic stress, where the interplay between RecA and LexA proteins plays a pivotal role. RecA oligomerizes on ssDNA, triggering LexA to undergo autoproteolysis and lose its repressive function on SOS genes. Understanding the structural aspects of this RecA-LexA interaction is crucial for developing inhibitors of the SOS response. An integrative structural biology approach was used to study the Pseudomonas aeruginosa SOS response. X-ray crystallography and electron microscopy revealed the structures of LexA autoproteolytic domain and the RecA/ssDNA complex. Cryo-EM showed the LexA-RecA/ssDNA complex structure, shedding light on the interaction mechanism. Nanobodies developed through llama immunization and phage display were found to be potent LexA inhibitors. These nanobodies stabilize LexA in an uncleavable conformation, reducing SOS gene expression in bacterial cells under antibiotic stress. X-ray structures confirmed nanobodies' ability to enhance LexA inhibition. This research not only advances understanding of the SOS response but also offers new possibilities for antimicrobial strategies.

References:

[1] Maso L, Vascon F, Chinellato M, Goormaghtigh F, Bellio P, Campagnaro E, Van Melderen L, Ruzzene M, Pardon E, Angelini A, Celenza G, Steyaert J, Tondi D, Cendron L. (2022) *Structure* 30, 1479.
[2] Bellio P, Mancini A, Di Pietro L, Cracchiolo S, Franceschini N, Reale S, de Angelis F, Perilli M, Amicosante G, Spyrakis F, Tondi D, Cendron L, Celenza G. (2020) *Life Sci.* 241, 117116.
[3] Bellio P, Di Pietro L, Mancini A, Piovano M, Nicoletti M, Brisdelli F, Tondi D, Cendron L, Franceschini N, Amicosante G, Perilli M, Celenza G. (2017) *Phytomedicine* 29, 11.

DIFFUSE SCATTERING AND NANOSCALE CORRELATIONS IN QUANTUM MATERIALS

Damjan Pelc[1]

[1] Department of Physics, Faculty of Science, University of Zagreb, Croatia; *E-mail:* dpelc@phy.hr

Structural inhomogeneity at the nanoscale is often present in quantum materials, and can play an important role in determining their electronic properties. However, it is a major challenge to experimentally characterize bulk structural inhomogeneity, given that it is nearly invisible for standard diffraction techniques. Short-range structural correlations can be studied using diffuse scattering, yet this technique places specific, stringent requirements on both instrumentation and data analysis. The development of a new generation of dedicated synchrotron x-ray and neutron diffuse scattering instruments, coupled with big data analysis approaches, is now able to provide unprecedented insight into nanoscale inhomogeneity in crystalline materials. In this talk, I will briefly describe the capabilities of the leading x-ray and neutron diffuse scattering instruments, introduce the 3D-ΔPDF transformation that is used for visualization of atomic correlations in real space, and discuss our recent work on several prominent materials systems. The latter includes characterization of self-organized dislocation structures in plastically deformed $SrTiO_3$ and $KTaO_3$ crystals [1,2]; the unexpected discovery of nanoscale inversion-breaking correlations in superconducting $(Ba,K)BiO_3$ [3]; and measurements of local structural fluctuations in several families of cuprate high-temperature superconductors [4,5].

References:

[1] Hameed, S. et al. (2022). *Nat. Mater.* 21, 54.

[2] Khayr, I. et al. (2024). *arXiv*:2405.13249.

[3] Griffitt, S. et al. (2023). *Nat. Commun.* 14, 845.

[4] Pelc, D. et al. (2022). *Sci. Rep.* 12, 20483.

[5] Anderson, Z. W. (2024). *arXiv*:2405.10411.

Acknowledgement
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THE ROLE OF INTERMOLECULAR INTERACTIONS IN CHEMICAL PROCESSES

Catharine Esterhuysen[1]

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The most challenging aspect in understanding the properties of materials in the solid state is to identify the role that intermolecular interactions play in their behaviour. For instance, molecules ("guests") are taken up into porous materials ("hosts") as a result of the interactions between these species, while the manner in which they interact has an influence on the sorption ability of the porous material. So too for catalysts, where the first step in their mechanism of action is the formation of weak interactions between the metal centres and the catalytic substrates. Therefore, the the reactivity and selectivity or a catalytic reaction can be tuned by positioning of the substrate relative to the catalyst with the aid of weak intermolecular interactions.

In this presentation, several examples from our work will be used to show that computational methods allow us to explain the role that intermolecular interactions play in a range of chemical processes. In particular, I will focus on how interactions between water, CO_2 and other solvents influence the properties of porous materials, such as allowing the release of water down to temperatures as low as –70 °C [1], anomolous sorption behaviour [2] and solvatochromic effects [3]. The influence of hydrogen and halogen bonding and other weak interactions in catalysis [4] and crystal engineering [5,6] will also be demonstrated.

References:

[1] Eaby, A.C., Myburgh, D.C., Kosimov, A., Kwit, M., Esterhuysen C., Janiak, A. M., Barbour, L. J. (2023) *Nature*, 616, 288–295.
[2] Bezuidenhout, C. X.; Smith, V. J.; Bhatt, P. M.; Esterhuysen, C.; Barbour, L. J., (2015) *Angew. Chem. Int. Ed.* 54, 2079–2083.
[3] Bezuidenhout, C. X., Smith, V. J., Bhatt, P. M., Esterhuysen, C., Barbour, L. J. (2017) *Chem. Commun.* 53, 5618–5621.
[4] Moloto, B. P., Vermeeren, P., Dalla Tiezza, M., Esterhuysen, C., Bickelhaupt, F. M., Hamlin, T. A. (2022) *Eur. J. Org. Chem.* e202200722.
[5] Groenewald, F., Dillen, J., Raubenheimer, H. G., Esterhuysen, C. (2016) *Angew. Chem. Int. Ed.* 55, 1694–1698.
[6] Esterhuysen, C. (2024) *Cryst. Growth Des.* 24, 859–870.

SYNTHESIS AND STRUCTURE-PROPERTY RELATIONSHIPS OF SELECTED QUANTUM MATERIALS

Mirela Dragomir[1]

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A quantum material is one whose electronic or magnetic properties cannot be explained by classical textbooks, but require non-trivial quantum mechanical principles. These materials have the extraordinary potential to revolutionize energy transmission and data storage technologies. However, progress in this field depends crucially on the development of advanced experimental techniques for their synthesis and characterization. Moreover, the quantum effects in these materials are strongly influenced by their structure and dimensionality. In particular, the symmetry and topology of the lattice can dictate the ground state and overall behaviour of these materials.

In this talk, I will take a closer look at the intricate structure-property relationships of selected quantum materials. Using specific examples [1–5], I will discuss our recent efforts in the synthesis, crystal growth, and understanding the structure, electronic, and magnetic properties of these materials. I will also introduce our strategies for synthesizing metastable quantum systems [6].

References:
[1] Dragomir, M.; Dube, P. A.; et al. (2019). *Chem. Mater.* 31, 7833–7844.
[2] Dragomir, M.; Arčon, I.; et al. (2021). *Phys. Rev. Mater*. 5, 074403.
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[4] Arh, T; Zorko, A.; et al. (2022). *Nat. Mater*. 31, 7833–7844.
[5] Šibav, L.; Dragomir, M.; et al. (2024). *Inorg. Chem*. Submitted.
[6] Belak Vivod, M.; Dragomir, M.; et al. (2024). *J. Am. Chem. Soc*. Under review.

Acknowledgement
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SHORT ORAL PRESENTATIONS

X-RAY POWDER DIFFRACTION OF HIGH-ENTROPY ALLOYS

Anton Meden[1]

[1] University of Ljubljana, Faculty of Chemistry and Chemical Technology, Večna pot 113, SI-1000 Ljubljana; *E-mail*:t one.meden@fkkt.uni-lj.si

High-entropy alloys (HEAs) are alloys formed by mixing equal or relatively large proportions of (usually) five or more elements. The elements can be chosen so that the pairwise mixing enthalpies are small, so that a compositionally uniform solid solution should be formed. Thus, ideally, high-entropy alloys (HEAs) should be single phase with randomly mixed atoms of the constituent elements at crystallographic sites of a (simple) crystal structure. In such cases, X-ray powder diffraction (XRPD) is an efficient tool to

1. verify phase purity
2. determine the structure type
3. determine the exact unit cell parameters
4. estimate the size and strain of the coherent scattering domains.

Often HEAs are in fact quite complex multiphase mixtures and in such cases XRPD is an essential tool for phase identification and quantification. For the identified phases, points 2 and 3 above also apply, while point 4 is only possible for dominant phases.

The reliability of the results is greatly increased when XRPD methods are used together with scanning electron microscopy (SEM) techniques (BSE imaging and EDS grain analysis).

The above is illustrated with examples (as in Fig. 1).

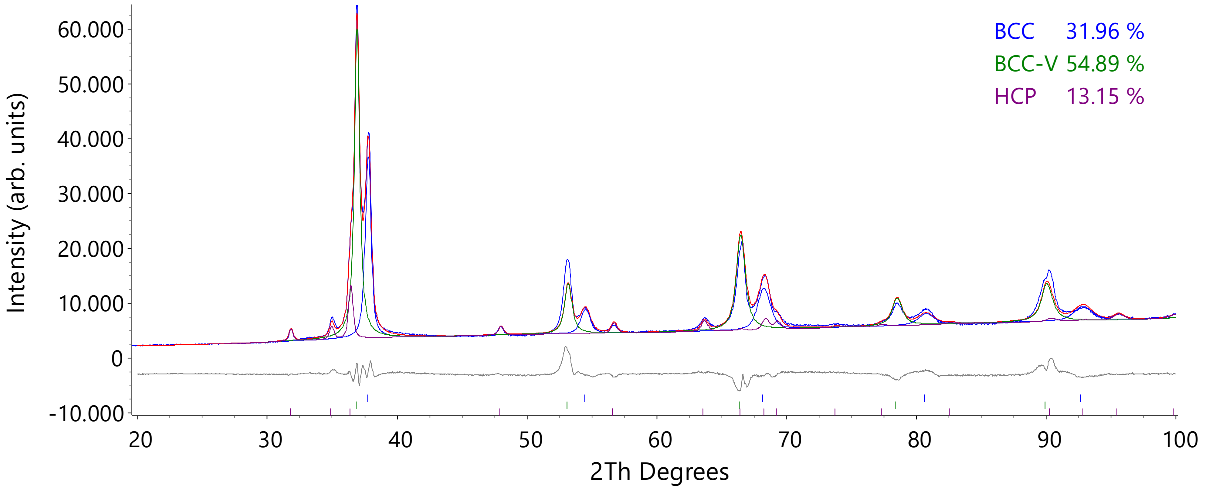

Figure 1. Rietveld plot of ScHfNbTaZr showing the contributions of the three phases to the measured diffraction pattern and their weight fractions.

Acknowledgement
All materials, mentioned in this contribution were supplied by prof. dr. Janez Dolinšek from the Faculty of Mathematics and Physics and Jožef Stefan Institute, Ljubljana, Slovenia, for which he is gratefully acknowledged.

XRD “MICROSCOPY”: A CASE OF IN-*SITU* FORMATION OF THE AL–ZN SOLID SOLUTION

Željko Skoko[1], Jasminka Popović[2] and Stanko Popović

[1] Department of Physics, Faculty of Science, University of Zagreb, Bijenička c. 32, 10000 Zagreb, Croatia; *E-mail:* zskoko@phy.hr
[2] Institute Ruđer Bošković, Bijenička c. 54, 10000 Zagreb, Croatia

~ In tribute to our most supportive mentor, altruistic teacher, amazing crystallographer, beloved professor Stanko Popović ~

Age-hardenable aluminum alloys possess several favorable properties, e.g. high electrical conductivity and hardness compared to their relatively low density and hence their technological importance, especially in aeronautics and automobile industry. In recent years, concern about usage of aluminum-based materials as the energy storage or conversion material has increased. The Al–Zn system, among binary aluminum alloys, is exceptionally attractive and suitable for mechanism studies and investigations of phase transitions kinetics in solid solutions.

Formation of the Al–15 at% Zn solid solution was followed by in-situ high-temperature X-ray powder diffraction (XRPD) measurements. It was found that the temperature of 200 °C marked an onset of the dissolution of Zn atoms in Al matrix, while the solid solution was formed at 300 °C. Change in the shape of Zn precipitates during the solid solution formation was analyzed by the *XBroad* program. The program provides detailed information about changes in size and/or transformation of shapes during different crystallization/dissolution processes without any prior information on structural features of the system under study. It was demonstrated that the *XBroad* program is an excellent tool for the quick and effective microstructural analysis easily used by material science community regardless of their background in the field of crystallography [1, 2].

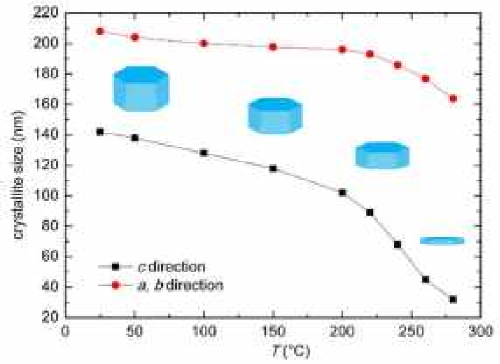

Figure 1. Changes of crystallite dimensions of Zn precipitates (along the *a*- and *c*-axis) during formation of the solid solution, from RT to 280 °C.

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STRUCTURE DISTORTION OF DIAMOND-POLISHED CUPRITE SURFACE LAYERS AND ITS IMPACT ON RAMAN SPECTRA

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Cuprite, Cu_2O, with its well-known cubic crystal structure type, has long been known to exhibit anomalous optical anisotropy of diamond-polished surfaces, when observed under crossed polarizers in reflected-light microscopy [1]. In contrast, natural untreated crystal faces and carefully chemo-mechanically polished surfaces (using MasterMet, i.e., an alkaline silica polishing fluid) show correct optical isotropy. As a matter of symmetry, (100) and (111) faces (normal to the 4- and 3-fold rotational axes) are not sensitive to this effect. Eventually, the effect has been explained by a deformed non-crystalline surface layer caused by mechanical diamond polishing that inhibits electron back-scatter diffraction (electron channeling patterns) in scanning electron microscopy [2].

This anomalous optical effect has been observed and studied in the last decades on a number of hard and brittle ore minerals such as pyrite, marcasite, gersdorffite, magnetite, chromite, and others [3, 4]. In addition, Raman spectra of these minerals were shown to consistently exhibit blue-shifted (i.e., towards higher wavenumbers) and broadened modes in case of mechanical diamond polishing. This behavior indicates shorter/stronger bonds and a higher degree of structural disorder. For the present confocal micro-Raman spectroscopic investigation of cuprite a blue Ar-ion laser (488 nm) was employed, because blue is reflected back from the uppermost surface layers (R = 30%) while red light (R = 22%) penetrates the red cuprite crystals into deeper bulk regions. Focussing was adjusted slightly above the surface.

In agreement with previous Raman studies of ore minerals (see above), the cuprite spectra exhibit a blue-shift of Raman modes of up to 20 cm^{-1} in mechanically diamond-polished surfaces, and MasterMet-polished surfaces behave like natural untreated crystal faces (Fig. 1).

In contrast to previous Raman studies, the mechanically diamond-polished surfaces do not cause broadened Raman modes. Amazingly, Raman modes get even sharper, which indicates a better degree of structural order in the upper deformed surface layers.

In general, these surface defects can corrupt quantitative information derived from spectral investigations or even hamper correct fingerprinting and the subsequent successful use of a Raman database.

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STRUCTURAL DETERMINATION OF NOVEL PYRAZOLONE AND DIAZEPINE DERIVATIVES

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Investigation of unsaturated bicyclic systems containing nitrogen holds significant importance in medicinal and biological chemistry due to their pronounced biological activity and prevalence in natural products. Among these systems, pyrazolo[1,2a]pyrazolones are of particular interest, because of their use as peptidomimetics, specifically as Lilly's γ-lactam antibiotics.[1] Although these compounds absorb visible light, only a few photochemical transformations of these scaffolds are known to date.

In this work, we present novel visible-light-induced transformations of pyrazolo[1,2-a]pyrazolones and structural determination of the synthesized products. Upon irradiation with visible light pyrazolo[1,2-a]pyrazolones undergo transformation into pyrazolo[1,2-*a*][1,2]diazepines. Subsequent irradiation with UV A light induces a disrotatory 4-π-electrocyclization yielding 5,5,4-tricyclic products. Although this transformation could theoretically afford four 5,5,4-tricyclic isomers, only one isomer is generated. The high stereoselectivity of this transformation is attributed to the preferential conformational stability of one of the two 1,2-diazepine isomers, in which diazepine products can exist in solution. The conformational outcome in 5,5,4-tricyclic products is further determined by their relative conformational stability, as predicted by DFT calculations. The structures and relative configurations of 1,2-diazepine and 5,5,4-tricyclic products were unambiguously determined by X-ray diffraction. The structural determination results were furthermore confirmed with 1D and 2D NMR analysis, where the coupling constants aligned perfectly with the torsion angles obtained from the X-ray diffraction analysis.

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BRIDGING THE GAP BETWEEN ELECTRON AND X-RAY DIFFRACTION

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Structure determination on ever smaller and more weakly diffracting crystals is one of the biggest challenges in crystallography. Traditionally, in-house X-ray crystallography covers sample sizes down to a lower limit of approximately 50 µm [1]. Consequently, electron diffraction is receiving a lot of attention, as it promises structure determination on significantly smaller samples. However, while micro-ED can cope with samples in the nm range up to approximately 1 µm, the refined structure models are less accurate compared to X-ray data [2]. Furthermore, the preparation of suitable sub-µm samples is often a challenge, whereas few micrometers sized crystals would be readily available. Therefore, equipment for X-ray structure determination closing the gap for samples between 50 to 1 micrometer in size would be highly desirable.

Exciting developments and latest innovations in X-ray source and detector technology enable the crystallographer to bridge this gap. Crystal sizes in the sub-10 µm range are now routinely accessible by modern instrumentation, while at the same time retaining the convenience and accuracy of single crystal X-ray structure determination. This will be highlighted by comparing single crystal X-ray diffraction data collected on micro crystals and recently published micro-ED data [3].

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ZINC(II)-BASED COORDINATION CHEMISTRY OF FUROSEMIDE: FROM COMPLEXES TO COORDINATION POLYMER

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Furosemide is a powerful and widely used sulfonamide diuretic for the treatment of various cardiovascular and renal conditions. Although this drug has been used for decades, some aspects of its mode of action remain unclear [1]. The structure of furosemide (Fig. 1) allows coordination to metal ions, so it is surprising that only two crystal structures of coordination compounds with furosemide as a ligand can be found in the Cambridge Structural Database [2]. To fill this gap, our recent studies on zinc(II) coordination chemistry [3] were extended to include biologically active ligands starting with furosemide. First, a simple coordination compound with the composition $[Zn(fur)_2(NH_3)_2]$ was prepared, where fur$^-$ stands for deprotonated furosemide. When quinaldinate (abbreviated as quin$^-$) was introduced into the reaction mixture under harsher conditions, a one-dimensional coordination polymer with the composition $[Zn_3(fur)_2(quin)_4]_n.2CH_3OH$ (Fig. 1) was obtained. Quinaldinate acts as a bridging ligand and connects the metal centers. The structure features two types of zinc(II) ions: one has four monodentate quinaldinates in a tetrahedral arrangement and the other is penta-coordinated with two quinaldinates in *N*,*O*-bidentate chelating mode and a deprotonated furosemide in monodentate coordination *via* a carboxylate oxygen.

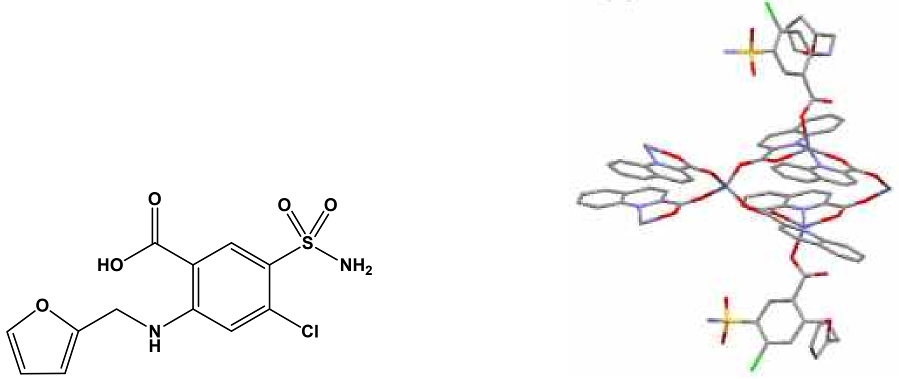

Figure 1. Structure of furosemide (left) and a repeating unit in the coordination polymer $[Zn_3(fur)_2(quin)_4]_n$. (right).

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Acknowledgement

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ZINC(II) COORDINATION POLYMER CONTAINING QUINALDINATE AND 2-HYDROXYPYRIDINE LIGANDS

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In continuation of the studies on the [Zn(quin)$_2$(H$_2$O)] (quin$^-$ stands for the anionic form of quinaldinic acid) reactions with selected *N*- and *O*-donor ligands, a zinc(II) starting material was reacted with a series of hydroxypyridine ligands.[1] Using an excess of 3-hydroxypyridine (3-py-OH), [Zn(quin)$_2$(3-py-OH)$_2$] was formed with 3-py-OH ligands bound *via* the nitrogen atom. In the case of 4-hydroxypyridine, its other tautomer, *i.e.* 4-pyridone, acted as a ligand and [Zn(quin)$_2$(4-pyridone)], a monocomplex, with 4-pyridone bound *via* oxygen atom was obtained. With 2-hydroxypyridine also known to display tautomerism, a similar behaviour to 4-hydroxypyridine was expected. However, instead of a mononuclear complex with 2-pyridone, a polymeric compound with the [Zn$_{2.5}$(quin)$_4$(2-pyridone)(2-py-O)]$_n$ (2-py-O$^-$ denotes 2-pyridonate) composition was formed. Apparently, 2-pyridone underwent partial deprotonation and the resulting 2-pyridonate coordinated *via* its both donor atoms to two adjacent metal ions. With the agency of the bridging 2-pyridonate and quinaldinate ligands, the zinc(II) coordination units were linked into infinite chains (Fig. 1). The resulting connectivity pattern classifies [Zn$_{2.5}$(quin)$_4$(2-pyridone)(2-py-O)]$_n$ as a coordination polymer (CP).[2]

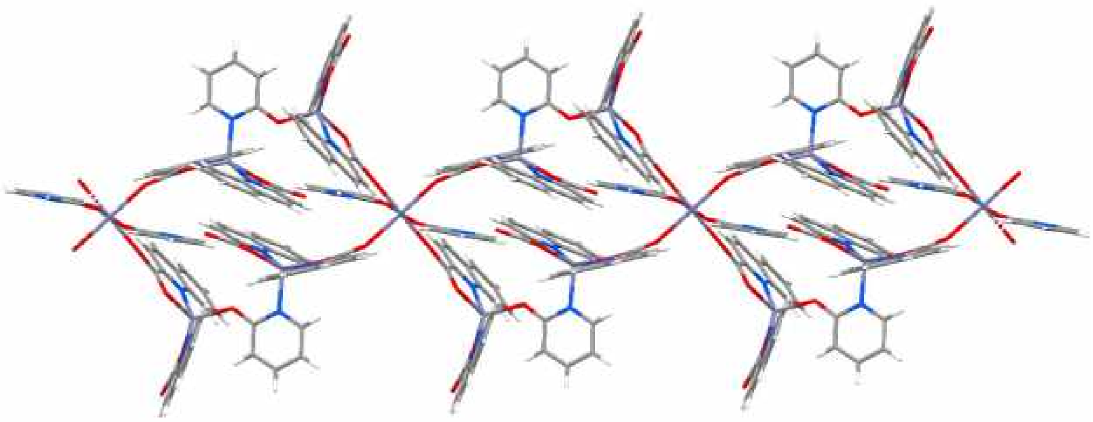

Figure 1. Section of a coordination polymer (CP) [Zn$_{2.5}$(quin)$_4$(2-pyridone)(2-py-O)]$_n$.

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CRYSTALS UNDER THE SPOTLIGHT – DISCOVERING THE POSSIBILITIES OF CRYSTALS' DYNAMIC BEHAVIOUR

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By combining the best of both worlds – adaptability to various stimuli from soft biological systems, together with ordered structural arrangement of crystals, dynamic crystalline materials attract the attention of not only crystallographic but also broader scientific community. [1] Even though an increasing number of reports describing mechanically compliant crystals emerged in the last few years, they continue to surprise with novel and astonishing functional properties. The desirable fusion of physical and mechanical performances of these crystals opens a plethora of possibilities for their potential application in emerging technologies that are yet to be discovered. [2] An additional advantage of crystalline materials is the ability of controlled structure modification, which in turn enables fine-tuning of the specific material's property. It was demonstrated that only slight modification in molecular structure, which has a subtle impact on supramolecular architecture, leads to a major change in the type and degree of the mechanical response. [3–6]

Here we focus on the two coordination compounds of similar composition, a 1-D polymer of cadmium(II) and 1-D polymer of copper(II), both with bromide and 3,5-dichloropyridine ligands. Although the only difference between the observed compounds is in the type of octahedrally coordinated metal centre, some obvious differences can be observed in their room-temperature molecular and crystal structure. Structural differences are reflected in the crystals' mechanical properties, as both compounds display mechanically stimulated flexible responses, ranging from elastic to plastic bendability of different degree. In addition to the mechanically stimulated response, crystals of cadmium(II) coordination polymer displayed reversible single crystal-to-single crystal (SCSC) upon heating - cooling cycles, followed by abrupt crystal jumping. The combination of mechanically and thermally triggered dynamic motion of a crystal provides a solid ground for further investigation of this family of compounds for possible applications in emerging technologies.

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Acknowledgement

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SURPRISING STRUCTURE OF A RHENIUM(I) COMPLEX

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In recent years, rhenium(I) tricarbonyl complexes have been trending topic of research. Rhenium(I) tricarbonyl complexes show promising biological and catalytic activity. They are of particular interest due to their spectroscopic properties, as they can be used for both diagnostic and therapeutic applications [1,2].

Pyrithione is a naturally occurring compound that has been known for a long time. Pyrithione forms simple binary coordination compounds with most metals in the periodic table. The best-known coordination compound is with zinc. Bis(1-hydroxy-2(1*H*)-pyridinethionato) zinc or more commonly known as zinc pyrithione has been used for many years in anti-dandruff shampoos and outdoor paints as it has a strong antimicrobial effect [3,4].

Over the last couple of years, our research group has prepared various pyrithione analogues and also various *fac*-tricarbonyl rhenium(I) complexes with mostly *N*,*N*-type ligands [5]. We have extensively investigated pyrithione and its analogues with various metals as potential anticancer agents. Promising results using pyrithione ligands with various metals prompted us to also prepare *fac*-tricarbonylrhenium(I) complexes with different pyrithiones. We synthesised and characterised the compounds we prepared. We also succeeded in obtaining single crystals and their structures were determined by X-ray diffraction. During the NMR stability measurement, we were surprised by the formation of dark crystals, and the X-ray diffraction revealed an even more astonishing structure of the compound.

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COBALT(III) COMPLEX WITH IN SITU FORMED LIGAND DERIVED FROM 2-PYRIDINEMETHANOL

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With their two possible coordination sites and many different possible coordination modes, simple pyridine alcohols are interesting ligands for use in coordination chemistry. On the other hand, the features of cobalt coordination compounds span from catalytic to redox.

Focusing on the reactions of 2-(hydroxymethyl)pyridine (2hmp) with cobalt(II) chloride in acetonitrile, a mixture of two differently coloured crystals formed. In addition to the formation of orange crystals of *trans*-$[Co(2hmp)_2(OH_2)_2]Cl_2$, several darker brown crystals also appeared. The structural analysis has shown that the darker crystals represent Co(III) coordination compound in which the homoleptic coordination cation with two scorpionate N,N,O-ligands coordinated to the central atom in a *fac* mode is neutralized by the chloride anion. The process of C-C bond and diol formation from 2hmp at ambient conditions has already been observed but remains unexplored [1].

For the determined crystal structure, the Hirshfeld surface analysis was additionally performed.

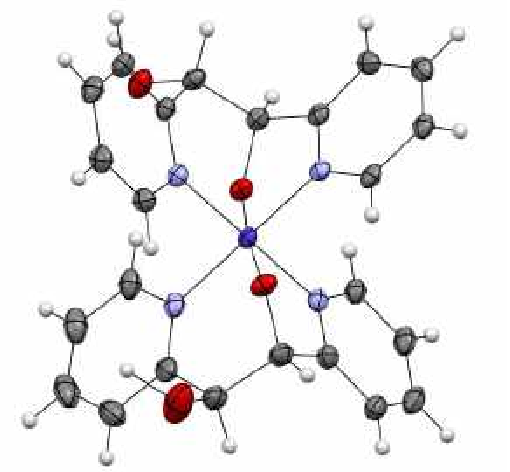

Figure 1. ORTEP representation of coordination cation with in situ formed (N,N,O)-scorpionate ligand.

References:

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Acknowledgement

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INVESTIGATING THE GLASS-FORMING REGION IN SODIUM PHOSPHATE-NIOBATE-BASED GLASS SYSTEMS

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With the growing significance of amorphous materials in energy storage applications [1], sodium-phosphate-based glasses and glass-ceramics are emerging as promising solid-state electrolytes for sodium batteries due to their high ionic conductivity [2]. These materials are highly tunable through compositional modifications, with oxides like Al_2O_3, ZnO, and Nb_2O_5 significantly improving chemical durability, thermal behaviour, and electrical conductivity by forming mixed P–O–M (M = Nb, Al, Zn) bonds [3–6]. This study focuses on glass-forming region (GFR) and investigates thermal, structural, and electrical properties within the ternary Na_2O-Nb_2O_5-P_2O_5 glass system. Additionally, the effects of incorporating small amounts of Al_2O_3 and ZnO are investigated. The glasses are synthesized via the conventional melt-quenching method, and the GFR is determined. Obtained vitreous material is further studied utilizing a variety of techniques, including Raman, infrared, and impedance spectroscopies and differential thermal analysis. These results introduce novel glass systems with customizable properties, providing valuable insights for advancements in materials science and technology.

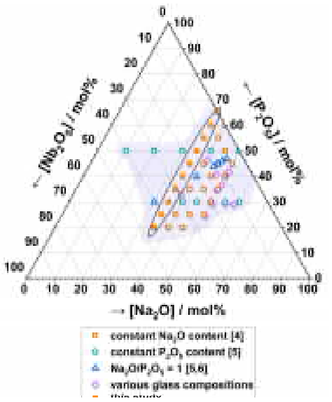

Figure 1. Ternary diagram showing the glass-forming region of the Na_2O-P_2O_5-Nb_2O_5 glass system, based on literature data. Glasses synthesized in this study are marked with black circle.

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SUPRAMOLECULAR DESIGN FOR BIOMIMETIC MODEL COMPLEXES: CRYSTALLOGRAPHIC CONSIDERATIONS FROM A NON-CRYSTALLOGRAPHER

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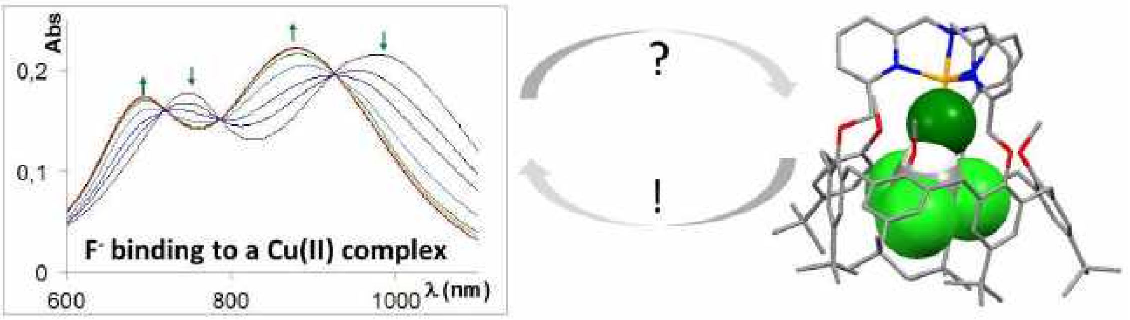
The combination of coordination chemistry and supramolecular chemistry makes it possible to propose biomimetic models presenting the key characteristics of metallo-enzymes. The design of a tailored environment around a metallic centre allows to finely modulate molecular recognition or reactivity properties.[1] The study of these dynamic supramolecular systems in solution sometimes leaves open questions to which crystallographic analysis can bring answers. Through different examples taken from the research carried out within our team, we will illustrate how a comparison of data obtained in solution and in the solid state leads to a description as precise as possible of the parameters controlling a molecular process.[2, 3, 4, 5, 6.]



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All the colleagues cited in the references who participated to the different projects herein discussed. Financial support from Croatian Science Foundation (IP-2020-02-3786 and IP-2018-01-5475).

FLUORESCENT MOLECULAR PROBES FOR ALZHEIMER'S DIAGNOSIS: SYNTHESIS, CRYSTAL STRUCTURES AND BIOLOGICAL EVALUATION

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The development of fluorescent dyes is crucial for the visualization of amyloid β (Aβ) plaques, a hallmark of Alzheimer's disease (AD) [1,2]. In this study, we synthesized a series of new fluorescent probes to explore their structure, optical properties, and binding affinity to Aβ.

The probe's design includes central π-system scaffolds with electron-donating (EDG) and electron-withdrawing groups (EWG) as end caps. The crystal structures of four compounds were determined using low-temperature single-crystal X-ray diffraction. In these structures, nitrogen atoms in heteroaryl rings and the nitrile group act as hydrogen-bond acceptors, while hydroxyl groups serve as hydrogen-bond donors. This interaction is evident in the formation of hydrogen-bonded dimers in the crystal structures of two compounds.

To evaluate the suitability of these fluorophores for bioimaging, we measured absorption, emission, and excitation spectra along with quantum yields in solvents of varying polarities, including *n*-hexane, dichloromethane, methanol, acetonitrile, and HEPES buffer solution.

Additionally, we assessed the binding affinity of the fluorescent probes to Aβ *in vitro*, *in cellulo*, and on *postmortem* brain slices from AD patients. The probes selectively bound to Aβ fibrils, with interactions proposed through docking studies and molecular dynamics simulations. These findings offer valuable insights into the potential of these probes as diagnostic tools for AD [3].

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Acknowledgement

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Co(II) COORDINATION BY CAPPED CALIX[6]ARENES

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Investigation of the potential of series of calix[4]- and calix[6]arene ligands to bind to a variety of DNA/RNA chains had revealed that the charge present in the binder plays a pivotal role in the recognition/binding process [1]. In order to examine the possibility to replace the intrinsic ligand charge by the one emanating from the coordinated cation, we have undertaken a broader study of interaction of the calixarene-based binders with series of transition metal cations [2].

TMPA or TREN cap grafted to the large rim of a calix[6]arene macrocycle *via* three suitably designed linkers provide a powerful tripodal tetradentate *NNNN* coordination core, enabling the metal cation, once coordinated, to have one free coordination site oriented towards the hydrophobic calixarene cavity and capable of intra-cavity binding of an (exchangeable) ligand.

Reactions of calix-TMPA/calix-TREN ligands with $\mathrm{Co(ClO_4)_2}$ in the presence of acetonitrile and subsequent crystallization of the so prepared complexes lead to the formation of single crystals of $[\mathrm{Co^{II}(MeCN)}\textbf{Calix-TMPA}^{\mathbf{Me}}](\mathrm{ClO_4})_2$ (**1**), and $[\mathrm{Co^{II}(MeCN)}\textbf{Calix-TREN}^{\mathbf{Me}}][\mathrm{ClO_4}]_2$ (**2**). When the pink crystals of **2** are exposed to air over a prolonged period of time, the colourless crystals of its isostructural counterpart $[\mathrm{Co^{II}(OH{\cdots}OH_2)}\textbf{Calix-TREN}^{\mathbf{Me}}][\mathrm{ClO_4}]$ (**3**) are formed. In all complexes, Co(II) sits in the centre of a slightly distorted trigonal bipyramide, with four donor atoms emanating from the tripodal cap, and the fifth coming from the intra-cavity bound guest: acetonitrile (in **1** and **2**) or hydroxide (in **3**). Complex **1** crystallizes with two conformational enantiomeres in the asymmetric unit. In all complexes, intra-cavity guest coordination is supported by a network of hydrogen bonds. Intriguingly, when TMPA cap is deprived of the calix[6]arene cavity, it dispays a peculiar Co(II) coordination as displayed in $[\mathrm{Co^{II}}\textbf{TMPA}^{\mathbf{CH2OH}}](\mathrm{ClO_4})_2$ (**4**). Here, heptacoordinated Co(II) lies in the center of a distorted capped trigonal prism. $\textbf{TMPA}^{\mathrm{CH2OH}}$ acts as a heptadentate ligand in which all available donor atoms are employed in the Co(II) coordination.

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EXPLORATION OF THE TERNARY SYSTEM CUBR – HBR – DABCO

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Complexes of copper(I) halides and organic ligands represent a group of potentially new catalysts for different organic reactions and semiconductor materials, which could be used in various fields of optoelectronics (e.g. LED lights, photovoltaic cells...) [1–3].

We decided to investigate the ternary system of CuBr – HBr – DABCO which is still relatively unexplored. In the CSD database (version 5.45, November 2023) we were able to find only 4 entries (CCDC ref. code: BICHED, KOLZET, QOYPAX in QOYQIG) that correspond to the system in question [4].

Using solvothermal (in acetonitrile) and electrochemical synthesis (in acetonitrile and ethanol) we systematically investigated the ternary system. Up to now, we were able to find 7 new structures. Short overview of the crystal structures together with graphs of where individual phases appear in ternary system will be given at the conference.

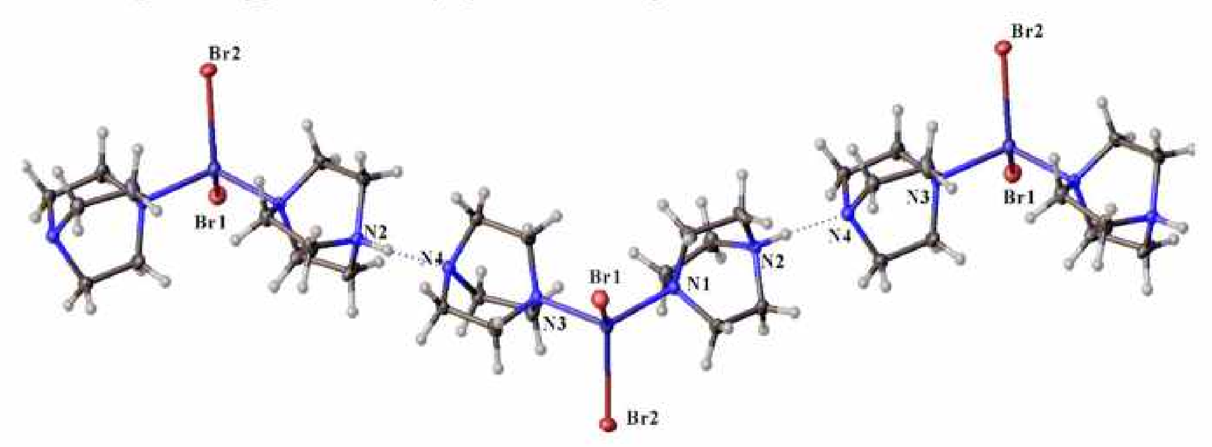

Figure 1. Picture of complexes (HDABCO)$CuBr_2$(DABCO) connected with hydrogen bonds.

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Acknowledgement

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HYDROGEN-BONDED COCRYSTALS OF TRIPHENYLARSINE OXIDE

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Cocrystals can be defined as crystalline materials containing at least two different molecular and/or ionic compounds, held together by non-covalent interactions (hydrogen bonds, halogen bonds, van der Waals forces) [1]. Hydrogen bonds have been very well researched for the design of cocrystals, mainly because of their directionality and strength. Thus, even hydrogen-bond donor compounds that are liquid at ambient conditions can be crystallized as cocrystals [2].

Triphenylarsine oxide (Ph_3AsO) has long been overshadowed by its lighter analogue, triphenylphosphine oxide (Ph_3PO). Although both have similar electronic properties, Ph_3AsO has an advantage over its phosphorous analogue due to its larger dipole moment [3]. This leads to greater Lewis basicity of the more electron-rich oxygen atom of Ph_3AsO. A handful of studies have focused on the preparation of transition metal complexes of Ph_3AsO [4,5]. However, its ability to form hydrogen bonds has not yet been systematically explored.

Herein we report on several new hydrogen-bonded cocrystals with Ph_3AsO as hydrogen-bond acceptor and selected donors (Figure 1). The hydrogen-bond donor–acceptor interaction was studied in solution by NMR spectroscopy. The obtained cocrystals were analysed by vibrational spectroscopy (IR and Raman) and their crystal structures were determined by single-crystal X-ray diffraction. They are characterized by short O···O hydrogen-bond distances. Selected crystals were measured to high resolution (0.45 Å) for charge density analysis.

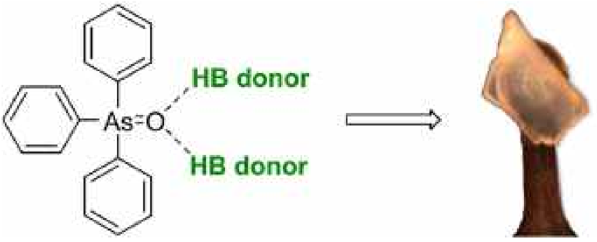

Figure 1. Representation of cocrystal formation between Ph_3AsO and hydrogen bond donors.

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PYRIDINE NITROGEN AS A BIFURCATED HALOGEN BOND ACCEPTOR IN COCRYSTALS OF 1,2-DIIODOTETRAFLUOROBENZENE AND PYRIDINE DERIVATIVES: CSD SURVEY, STRUCTURAL AND COMPUTATIONAL STUDY

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Perfluorinated iodoarenes are classical and to date the most used halogen bond donors in solid state chemistry, which, depending on the acceptor molecule, can form relatively strong and short halogen bonds.[1,2] The occurrence of bifurcated acceptor atoms in halogen-bonded cocrystals is extremely rare, and within the aforementioned group of donors they are dominantly formed with 1,2-diiodotetrafluorobenzene (**12tfib**). To further investigate this phenomenon, we have attempted to prepare cocrystals of **12tfib** with a series of monotopic pyridine derivatives, structurally characterize obtained compounds and quantitatively explore the formation of bifurcated halogen bonds in chosen systems by computational methods.

Cocrystallization of **12tfib** with monotopic halogen bond acceptors resulted in the preparation of 7 cocrystals in which the formation of I···N halogen bonds was observed. Prepared compounds have crystallized in two donor : acceptor ratios – 1:1 (in 4 cases) and 1:2 (in 3 cases). Cocrystals of 1:2 stoichiometry form 2,4,6-collidine (**246col**), 3,4-lutidine (**34lut**) and 4-*N*,*N*'-dimethylaminopyridine (**dmap**) which can all be considered as relatively strong bases. Acceptors 3-picoline (**3pic**), 2,6-lutidine (**26lut**) and 3,5-lutidine (**35lut**) as well as moderately strong base quinoline form cocrystals which are of 1:1 stoichiometry. In (**12tfib**)(**26lut**)and (**12tfib**)(**35lut**) molecules are connected by classical (monocentric) I···N halogen bonds resulting in formation of discrete supramolecular complexes. On the other hand, somewhat different supramolecular motives have been observed in crystal structures of (**12tfib**)(**3pic**) and (**12tfib**)(**quin**). In those structures pyridine nitrogen serves as acceptor of two I···N halogen bonds, while interconnection of molecules in crystal structures resulted in formation of centrosymmetric octamer or centrosymmetric tetramer, respectively. In both cocrystals bifurcated halogen bonds are asymmetric. The DFT calculation has shown the (**12tfib**)$_2$(**quin**)$_2$ tetramer to be a stable configuration in the gas phase, with the optimised geometry similar to that which exist in the crystal structure. Comparison of the halogen bond energy involved in formation of a (**12tfib**)$_2$(**quin**)$_2$ tetramer in the gas phase, with the energy would be involved in forming a classical (**12tfib**)(**quin**) dimer, has shown that the tetramer with the nitrogen atom acting as a bifurcated acceptor is generally a more favourable configuration than a pair of (**12tfib**)(**quin**) dimers.

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MORPHOTROPISM IN A SERIES OF HALOGEN BONDED COCRYSTALS DERIVED FROM AN ISOMORPHOUS SERIES OF *N*-(4-HALOBENZYL)-3-HALOPYRIDINIUM HALOGENIDES

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The development of crystal engineering has pointed to several methods by which series of isomorphous structures can be deliberately produced with some reliability through various design strategies. Such strategies include the preparation of inclusion compounds, and cocrystallisation using series of geometrically equivalent co-formers. The introduction of multicomponent crystals into the study of isomorphism raises however an interesting question – is there a predictable (and thus, for the purposes of crystal engineering, exploitable) relationship between the occurrence of isomorphism within a series of starting (simple) crystalline materials and its occurrence in a series of cocrystals derived from such a series of materials using the same co-former? In other words, to what extent will the morphotropic transitions within the series of cocrystals relate to those in the series of co-formers?

An obvious prerequisite for a detailed study into this question would be a sufficiently large series of isomorphous solids that could be made to form cocrystals in a predictable way. Recently, in a study of *N*-(4-halobenzyl)-3-halopyridinium halogenides, we found a large isomorphous series comprising no fewer than 11 members.[1] Therefore, cocrystals of *N*-(4-halobenzyl)-3-halopyridinium halogenides seemed to be an ideal platform for a further study of isomorphism in multicomponent systems. Following this idea, a series of 12 *N*-(4-halobenzyl)-3-halopyridinium halogenides (11 being isomorphous) have been crystallised with a neutral halogen bond donor, 1,4-diiodotetrafluorobenzene. A total of 18 crystalline products were obtained, 13 of which were 1:1 cocrystals, three were 2:1 cocrystals, and two were 2:3 cocrystals. The two 2:3 cocrystals were isomorphous, while the 1:1 cocrystals constituted 7 structural types, and the 2:1 cocrystals two structural types. In neither the case of 1:1 nor 1:2 cocrystals was there any correlation between the morphotropic transitions observed in the cocrystals or co-formers. However, in instances when both the coformers and the cocrystals were isomorphous, a discernible correlation between the corresponding isostructurality indices could be observed. On the other hand, considering that the dominant directional interaction in all the structures was halogen bond, a number of regularities could be observed, indicating that the distribution of the cocrystals among the structural types is, to a large extent, determined by the halogen bonding potential of the constituent cations and anions.[2]

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CRYSTAL STRUCTURE OF SPICY CAPSAICIN

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Capsaicin, $C_{18}H_{27}NO_3$, is the principal active compound from the capsaicinoid family of secondary metabolites present in the fruits of chilli pepper plants (Figure), which belong to the genus *Capsicum*. The spiciness of hot chillies is primarily attributed to capsaicin, which is a potent agonist of the TRPV1 heat receptor and thus a strong irritant. Chilli plants have been cultivated for several millennia, they are a staple spice of many cuisines around the world, and their popularity and consumption are increasing globally [1].

The Cambridge Structural Database [2] currently contains two entries for capsaicin, of which one reports only the unit-cell parameters [3], whereas the other is a crystal structure determination from synchrotron X-ray powder diffraction measurement [4].

In this work, a tiny single crystal measuring 30 × 60 × 70 μm^3 was selected from a commercial capsaicin sample and analysed by low-temperature single-crystal X-ray diffraction, employing Cu *K*α radiation. The resulting crystal structure (Figure), in which all H-atom parameters were freely refined, is in good agreement with the previously reported structure determination.

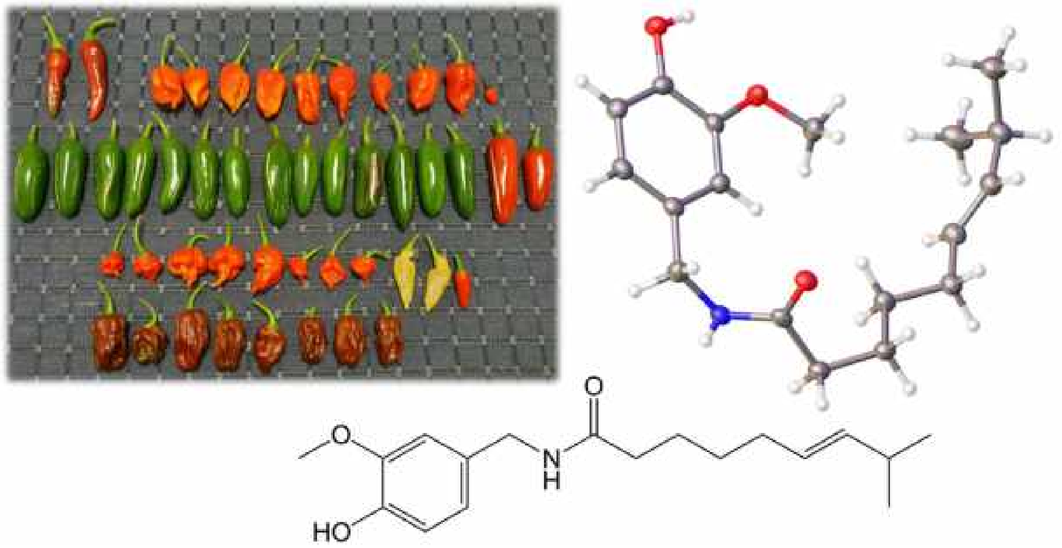

Figure 1. A colourful variety of different chili pepper cultivars and the crystal and molecular structure of capsaicin (50% probability ellipsoids).

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IMPROVING WORKFLOWS IN CRYSALISPRO WITH INTELLIGENT DEVICES AND AUTOMATION

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A short overview of the Rigaku Oxford Diffraction intelligent devices and novel automation tools in CrysAlisPro. The talk will show the latest implementation of automation in X-ray and electron crystallography.

NEW TERNARY GALLIDE $Zr_7Pd_{7-x}Ga_{3+x}$ ($0 \leq x \leq 1.8$)

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New ternary compound $Zr_7Pd_{7-x}Ga_{3+x}$ ($0 \leq x \leq 1.8$) was synthesized by arc melting the elements under argon and subsequent annealing the ingots at 870 K for 720 h. The polycrystalline samples were characterized by powder X-ray diffraction (XRD) and the crystal structure of compound was defined from the $Zr_7Pd_7Ga_3$ single crystal XRD data. $Zr_7Pd_7Ga_3$ crystallizes with the ternary ordered version of Zr_7Ni_{10} type of structure with the statistical mixtures of palladium and gallium atoms in the three crystallographically independent nickel sites, Pearson's symbol *oS*68, space group *Cmce*, $a = 12.997(3)$, $b = 9.6231(17)$, $c = 9.6302(15)$ Å, $Z = 4$, $R1 = 0.033$, $wR2 = 0.067$ for 719 unique reflections with $I_o > 2\sigma(I_o)$ and 48 refined parameters. The crystal structure of $Zr_7Pd_7Ga_3$ complies of a 3D $[Pd_7Ga_3]_\infty$ framework consisting of sinusoidal *M* layers (*M* = statistical mixture of Pd and Ga atoms in ratio of 7:3, interatomic distances $d_{M\text{-}M}$ vary from 2.763 to 2.774 Å). Such layers are stacked along the *b* axis with slightly longer *M*1-*M*2 (2.858 Å) and *M*3-*M*3 (2.872 Å) interlayer bonds. Zr atoms, to their equivalencies in $Zr_7Pd_7Ga_3$, are sandwiched between neighboring layers. Contrary to *M*–*M* and Zr–Zr distances, which are longer than the sum of metallic radii of atoms, the shortest Zr–*M* distances between 2.729 and 2.780 Å are significantly contracted. These data indicate the covalent bonding between Zr and *M*(Pd/Ga) atoms which is a remarkable feature of the structure. The homogeneity range and variation of the lattice parameters of the compound $Zr_7Pd_{7-x}Ga_{3+x}$ ($0 \leq x \leq 1.8$) have been refined from EDX and powder XRD data.

Crystal structure analysis of binary prototype Zr_7Ni_{10} and all known above forty binary R_7M_{10} and ternary $R_{7-x}M'_{x\pm y}M_{10\pm y}$ derivatives to Zr_7Ni_{10} has been done. The elemental composition and electronic configuration of ternary derivatives is very different. Alloying the third component *M'* with intermediate atomic radius compared with *R* and *M* elements stabilize this type of structure. Ternary compounds in which different atomic mixing *R*/*M'*, *M'*/*M*, *R*/*M* in Wyckoff positions occurs display some homogeneity ranges – smaller or larger. It is a remarkable feature of these ternary derivatives.

Electronic structure calculations and bonding analysis have been performed for an idealized model revealing that the stability of the crystal structure of $Zr_7(Pd,Ga)_{10}$ is mostly maintained by the Zr–Pd bonds, and enhanced by the doping of Ga at the Pd sites.

Acknowledgement

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CRYSTAL GROWTH, STRUCTURAL AND MAGNETIC CHARACTERISATION OF $ErTa_7O_{19}$ AND $Er_3Ta_{17}O_{47}$

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Rare-earth heptatantalates, RTa_7O_{19}, have been a subject of research since 1980s due to their high potential for applications in solid-state laser technologies and nonlinear optics [1]. Recently, a representative of the series, $NdTa_7O_{19}$, has also been recognised as a quantum spin liquid candidate, a highly sought form of exotic magnetism [2].

Motivated by this discovery, our attention has been focused on an erbium analogue, $ErTa_7O_{19}$ (Figure 1), which has not been described in the literature before. This compound could potentially exhibit an exotic magnetic ground state. Single crystals of $ErTa_7O_{19}$ have been successfully grown by flux method. A new phase, $Er_3Ta_{17}O_{47}$, has also been discovered to form during crystal growth. In this contribution, the crystal structure and the magnetism of $ErTa_7O_{19}$ and $Er_3Ta_{17}O_{47}$ will be discussed.

Figure 1. An as-grown $ErTa_7O_{19}$ single crystal.

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QUANTUM CRYSTALLOGRAPHIC STUDY OF *PANCAKE-BONDED* TCNQ RADICAL ANIONS

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Pancake bond is a specific, strong π-stacking interaction that occurs between rings of planar organic radicals. [1] It involves spin pairing of free radical's electrons which are shared between the two (or more) rings, hence the interaction is multicentric (2e/mc) and it has covalent character. [2] Study of these interactions involves exploring the nature of the chemical bond. Furthermore, since pronounced π-stacking motifs contribute to properties of the material, studying pancake bonds can be useful in developing the design of organic magnets and conductive materials. Crystals of salts with stacks of planar organic radicals that involve pancake bonding are of great interest in supramolecular chemistry as the foundation of new materials. [3] One of the most stable planar organic radicals suitable for the formation of such salts is 7,7,8,8-tetracyanoquinodimethane (TCNQ). [4]

In this work, we present a study of *pancake bonds* in three different salts of TCNQ: with 1,4-dimethyl-DABCO (**1**), *N*, *N*-dipyridylmethanium (**2**) and *N*, *N'*-dimethyl-4,4'-bipyridinium (**3**). Prepared compounds were thoroughly investigated by quantum crystallographic methods which reveal fine details of crystal and electronic structure. [5] TCNQ radical anions form complex patterns of dimers in **1**, trimers in **3** and tetramers in **2**. Structures with trimers and tetramers involve 2D arrays of TCNQ radicals. Trimers and tetramers form layers by stacking in a brick-wall pattern. Such patterns and short distances between rings enable extending the pancake bond and long-range interactions which is the core of the properties of materials. Electron density refinement reveals bond critical points between rings of radicals in all structures which is one of the confirmations of the presence of pancake bond.

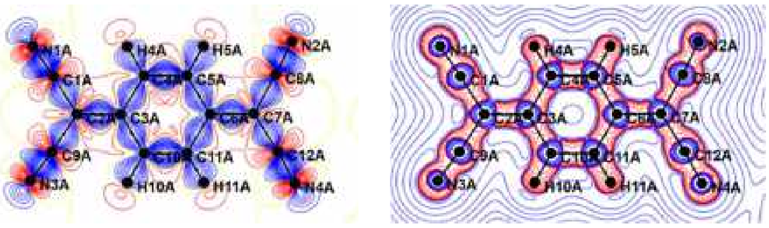

Figure 1. Deformation density maps in the mean plane of one TCNQ moiety in the crystal structure of **2** (left) and Laplacian of electron density in the mean plane of corresponding TCNQ moiety (right).

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Acknowledgement
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TWO-ELECTRON MULTICENTRE BONDING (*PANCAKE BONDING*): FROM DISCRETE DIMERS TO EXTENDED 2D ARRAYS

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Two-electron multicentre bonds (2e/mc or *pancake bonds*) are strong intermolecular interactions which occur between planar organic radicals [1]. They involve the pairing of spins of contiguous radicals due to the extension of the highest occupied molecular orbital (HOMO) between both radicals; this implies a significant covalent contribution to the total interaction, which often exceeds -15 kcal mol^{-1} [1]. Thus, 2e/mc bonds are some of the strongest intermolecular interactions, comparable to the strong hydrogen and halogen bonds. However, the electron pair is not localised, but distributed between two radicals, involving multiple centres [1]. Bulk properties of radical-based materials are defined by the degree of pancake bonding [1], so it is interesting not only from the fundamental aspects of nature of chemical bonding and intermolecular interactions, but also from an applicative point of view. Fine-tuning of this interaction may lead to the design of novel organic magnets and (semi)conductors.

Discrete (0D) pancake-bonded dimers or trimers are the most studied, and typically result in diamagnetic or antiferromagnetic properties of bulk samples [1]. These oligomers often stack by weaker (non-bonding) interactions. Extended 1D motives are characterised by (nearly) equidistant radicals with an interplanar separation shorter than 3.2 Å. The close contacts allow electron jumps between the rings and long-range magnetic ordering; therefore, the bulk materials are mostly semiconductive and antiferromagnetic [1]. Pancake bonding extending in 2D arrays was recently observed in salts of 7,7,8,8-tetracyanoquinodimethane radical anion (TCNQ) [4]. It involves spin interactions and electron transport in two directions (as evidenced by EPR spectroscopy) and conductivity up to 10^{-2} S cm^{-1} has been reported [2].

Here we present detailed quantum crystallographic studies of a series of 2e/mc-bonded radical systems, ranging from discrete dimers to 2D arrays, ranging from the simplest (dimers of TCNE radical anion) to 2D arrays comprised of TCNQ radical anions with a partial charge of $-1/2$ [2].

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HIRSHFELD ATOM REFINEMENT FOR METAL-ORGANIC FRAMEWORKS: ACCURATE ASSIGNMENT OF HYDROGEN ATOM POSITIONS AND DETAILED ANALYSIS OF GUEST DISORDER

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Metal-organic frameworks (MOFs) are microcrystalline materials, renowned for their applications in gas storage and separation, sequestration of atmospheric greenhouse gases, water purification and degradation of toxic agents, all of these applications stemming from the porous nature of these materials.[1,2] Detailed understanding of MOF host-guest chemistry relies on accurate determination of guest molecule positions within MOF pores, which has been proven challenging for X-ray diffraction methods.[3]

This presentation will report the first use of Hirshfeld atom refinement (HAR) for a MOF structure,[4] specifically for the *crb* polymorph of zinc imidazolate, colloquially known as ZIF-2.[5] The structural model obtained with the fragmentation HAR approach showed major improvements compared to the previous structures of ZIF-2 refined with the independent atom model (IAM). Unconstrained refinement of hydrogen atom positions resulted in C-H bond lengths comparable to standard neutron-diffraction values. Moreover, hydrogen atom displacement parameters were refined anisotropically. Finally, previously unreported disorder of the solvent guest molecules was identified, demonstrating how detailed structure analysis enabled by HAR method improves the description of guest species within MOF pores.

The presented approach offers high promise for the future structural analysis of newly-synthesized MOFs, including detailed analysis of guests within framework voids.

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Dr. Paul Niklas Ruth is thanked for the advice regarding the use of HAR with periodic wavefunction.

HIGH-PRESSURE AND TEMPERATURE STUDIES OPEN NEW INSIGHTS INTO TWO-DIMENSIONAL PEROVSKITE CsC[(NH2)3]PbI4

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Hybrid organic-inorganic perovskites have emerged as a revolutionary and highly promising class of materials with exceptional potential for optoelectronic applications [1,2]. Their unique combination of properties, such as high optical absorption coefficients, adjustable bandgaps, high photoluminescence quantum yields, long charge carrier lifetimes and diffusion lengths, has captured the attention of researchers and industries [1,2]. In recent years, particular focus has been directed towards studying the two-dimensional (2D) perovskites, which offer distinct properties compared to their three-dimensional counterparts, in particular strong quantum confinement.

Here, we present a comprehensive study of the effects of pressure and temperature on the structural and optical properties of $CsC[(NH_2)_3]PbI_4$. This material is a 2D perovskite that crystalizes in the orthorhombic system with the space group *Pnnm* [3]. The compound has a layered structure, where cesium and guanidinium cations are situated between the corner-shared PbI_6 octahedra layers.

The complex interplay between pressure, temperature, and the structural and optical properties of $CsC[(NH_2)_3]PbI_4$ will be demonstrated. Single-crystal X-ray diffraction (SCXRD), thermal analysis and optical spectroscopy techniques were used. While the crystallographic parameters of $CsC[(NH_2)_3]PbI_4$ were previously well established at room temperature and at 250 K [3], the pressure measurements as well as any observed phase transitions have not been reported before. A wider range of thermodynamic variables (200–380 K and up to 4.8 GPa) allowed us to observe unusual thermal expansion behavior, second-order phase transitions, and stability regions.

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HIGH THROUGHPUT AB INITIO CRYSTAL STRUCTURE PERDITION OF METAL-ORGANIC FRAMEWORKS WITH MACHINE LEARNING

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Metal-organic frameworks (MOFs) are a class of highly versatile materials with many exciting applications, such as gas storage and separation, water harvesting, catalysis and many more.[1] However, with essentially unlimited choice of MOF constituents, how shall we determine the optimum combination for our desired purposes? This presentation will demonstrate how high throughput *ab initio* crystal structure prediction (CSP) method can design new MOFs, which is then supplied for targeted experimental synthesis.

The initial work[2] to showcase the methodology of MOF CSP, utilised the *ab initio* random structure searching method (AIRSS) along with Wyckoff Alignment of Molecules (WAM) algorithm, successfully predicted several experimentally existing MOFs. In the subsequent work,[3] where our CSP method was applied to predict three novel hypergolic copper(II)-based zeolitic imidazolate frameworks (ZIFs) and their energetic properties. More importantly, our predicted low energy ZIF structures were fully validated by experimental synthesis. Nevertheless, there is still a limitation in our CSP method of using the accurate but computationally demanding periodic DFT calculations. Therefore, I will be presenting the alternative machine learning (ML) approaches, where well-trained ML potentials can perform rapid structures predictions to screen through thousands of highly polymorphic zinc imidazolate structures. So far, the ML potentials have already successfully predicted the experimentally existing ZIFs with *SOD* and *gis* topologies. Most crucially, performing ML structure predictions are around 1000-fold computationally cheaper compared to periodic DFT calculations, highlighting the great progress towards achieving high throughput structural design and property prediction of MOFs.

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A SEVENTH BLIND TEST OF CRYSTAL STRUCTURE PREDICTION METHODS

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Crystal Structure Prediction (CSP) – generating and ranking plausible crystal structures from a chemical diagram – is a rapidly evolving field, offering a diverse set of methods for predicting polymorphism of molecular crystals, directly informing the solid-form design process.

Since 1999 the CSP blind tests, a community initiative coordinated by the Cambridge Crystallographic Data Centre (CCDC), have provided CSP methods in development with an opportunity to validate and benchmark methodologies against unpublished data [1-6]. Here we present key results from the recent seventh blind test [7-8] which involved participation from 142 researchers from 28 groups in both academia and industry. CSP is now on the precipice of widescale accessibility and affordability with the increasing efficiency of methods for exploring structural space and ranking the stabilities of large numbers of crystal structures. These results demonstrate the tremendous improvement in predictive capabilities of CSP methods while highlighting urgent challenges for the community to address.

This talk provides an overview of the state of the art in CSP for those less familiar with the field, understanding applications and limitations of methods.

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STRUCTURE ELUCIDATION OF ORGANIC MOLECULES FROM EXPERIMENTAL SPECTROSCOPIC DATA USING SCHMARNICA

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Determining the structure of natural or synthetic organic molecules is a common task for chemists. If the compound in question crystallizes in a crystal suitable for an XRD study, structure determination can be straightforward. If this is not the case and you only have a very small amount of your compound, the process of structure elucidation becomes more difficult and can be labor intensive and time consuming. Despite widespread automation in various areas of science, the process of structure elucidation has remained largely unautomated since the development of chemoinformatics in the 1960s [1]. While considerable progress has been made in this field through structure annotation (WLN, SMILES, InChi), drug design and compound database creation, automating structure elucidation from experimental spectroscopic data without the use of existing databases, neural networks or user intervention remains an unresolved challenge [2, 3].

We have attempted to address this problem by developing an algorithm that mimics the structure elucidation process performed by a trained spectroscopist. We called it Schmarnica, and it differs from other similar systems under development in that it does not rely on database searches and comparisons. Instead, it takes a bottom-up approach and uses tabulated experimental spectroscopic data (IR, 1H, 13C NMR and MS) to generate structures of organic molecules. Our algorithm determines the connectivity of structural fragments from the given spectra using an analytical combinatorial approach and a graph search technique. With this information, it generates a list of possible molecular structures and orders them according to predefined rules, which facilitates the analysis of the spectroscopic data. Finally, the structures are visualized using the WolframAlpha computational knowledge engine. The developed Elucidator has a user-friendly web interface and is publicly available at http://schmarnica.si [4].

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SUPRAMOLECULAR ARCHITECTURES OF TWO *N*-ACYCLIC URACIL DERIVATIVES

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Worldwide, breast cancer is the second most common cancer, after lung cancer, and the most frequent cause of death from cancer in women [1]. Breast cancer is a complex and heterogeneous disease, characterized by deregulation of multiple cellular pathways, different morphology, and variable sensitivity to various treatments [2]. Despite significant progress in detection and treatment of breast cancer, metastatic breast cancer remains incurable. Recently, we reported synthesis and cytotoxic activity of nucleoside mimetics in order to explore the structure activity relationship of the C-5-heteroaryl (**1a**-**1b**) and alkynyl (**2a**-**2d**) uracil derivatives with the penciclovir-like side chain at N-1 of the pyrimidine scaffold, Figure 1 [3]. We succeeded to obtain single crystals of C-5-heteroaryl **1a** and alkynyl **2c** uracil acyclonucleosides, and in this contribution we present their X-ray structures. As they possess strong hydrogen-bonding donors and acceptors, the focus of this research will be on their supramolecular assembling.

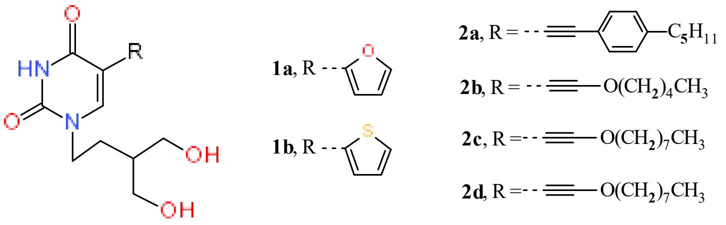

Figure 1. Molecular structures of the *N*-acyclic C-5-heteroaryl (**1a**-**1b**) and alkynyl (**2a**-**2d**) uracil derivatives

The molecules of **1a** are linked by strong hydrogen bonds, one N–H···O and two O–H···O, into tapes, which are then linked by three C–H···O hydrogen bonds and one C–H···π interaction into three-dimensional network. The same strong and weak hydrogen bonds (one N–H···O, two O–H···O and three C–H···O) participate in supramolecular assembling of **2c**. Compared to **1a**, hydrogen-bonded molecules are disposed in a *zig-zag* manner, but also form the complex network of hydrogen bonds and three-dimensional network.

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AROMATICS ANALYSER 2: A UNIFIED APPROACH TO WEAK INTERACTIONS

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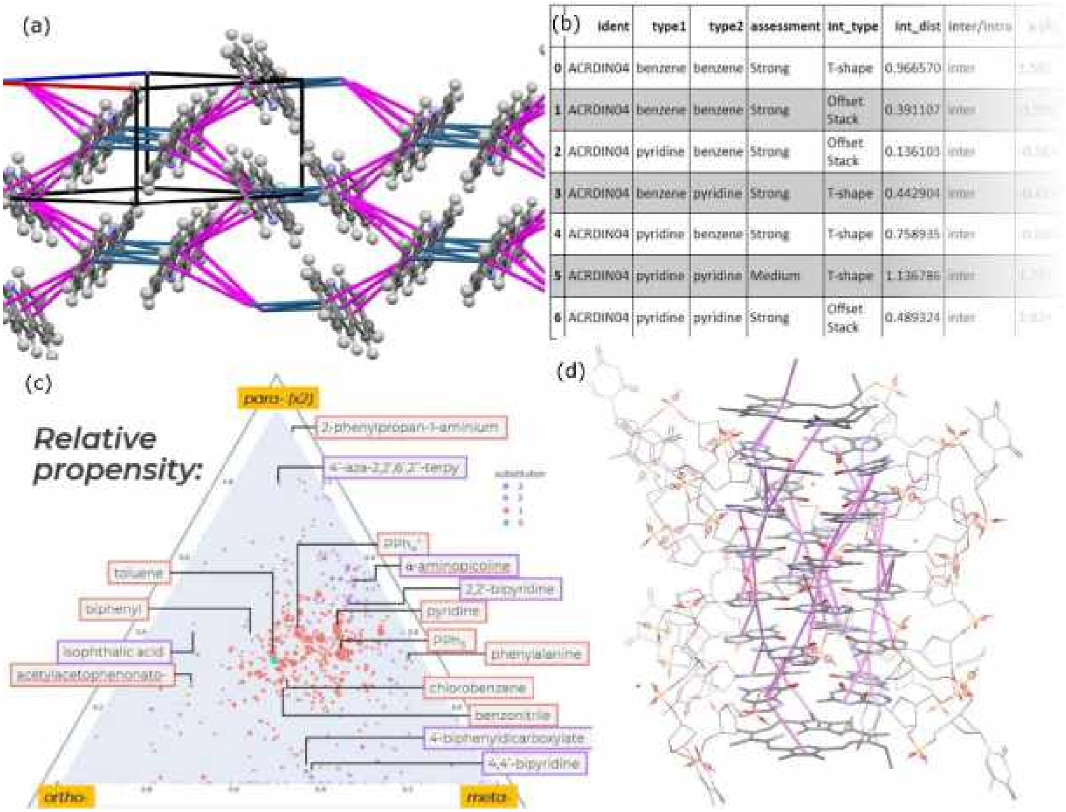
The interactions of aromatic systems are important in crystal form analysis and design, directing and informing properties of the crystalline solid state.[1] In presenting a new Aromatics Analyser (AA2),[2] we'll show how one can quantify these interactions across many heterocycle rings and interaction types, with a simple visualiser in Mercury and a notebook interface with the CSD Python API. This presentation will cover the evolution of Aromatics Analyser, and report some of the insights to polymorphism, structure direction and stability, bio-macromolecules and semiconductor design from analysis of millions of unique interactions in the CSD.



	ident	type1	type2	assessment	int_type	int_dist	inter/intra	[illegible]
0	ACRDIN04	benzene	benzene	Strong	T-shape	0.966570	inter	[illegible]
1	ACRDIN04	benzene	benzene	Strong	Offset Stack	0.391107	inter	[illegible]
2	ACRDIN04	pyridine	benzene	Strong	Offset Stack	0.136103	inter	[illegible]
3	ACRDIN04	benzene	pyridine	Strong	T-shape	0.442904	inter	[illegible]
4	ACRDIN04	pyridine	benzene	Strong	T-shape	0.758935	inter	[illegible]
5	ACRDIN04	pyridine	pyridine	Medium	T-shape	1.136786	inter	[illegible]
6	ACRDIN04	pyridine	pyridine	Strong	Offset Stack	0.489324	inter	[illegible]

Figure 1. **(a)** Visualised aromatic interactions between acridine molecules in ACRDIN04, and **(b)** tabulated results. **(c)** Aromatic substitution can direct aromatic interactions in the solid state, as differently substituted rings will have different ortho- meta- and para- directed aromatic interactions **(d)** This program can also analyse bio-macromolecules such as this G-quadruplex – N-methylporphyrinium complex (PDB: 6p45)

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A FIRST ATTEMPT TO USE CORRELATIONS IN TOURMALINE AS A THERMOMETER

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A new geothermometer is proposed based on the chemical composition of minerals from the tourmaline supergroup, which have the formula $XY_3Z_3(BO_3)_3[T_6O_{18}]V_3W$. An excellent correlation between the total charge of the *X*-site cations and the fluorine content in pegmatitic tourmalines was first reported by [1]. The *W* site is bound to three cations of the *Y* site. Where OH occupies the *W* site, the H points to the *X* site. The presence of F at the *W* site immediately adjacent to the XO_9 polyhedron increases the bond length distortion of this polyhedron [2]. A dependence of the *X*-site occupancy to the formation conditions during tourmaline crystallization was already suggested by [3]. Over the last 15 years, several excellent correlations between *X*-site charge and F content have been observed in tourmalines from various pegmatites, such as that reported by [4]. On that correlation, all zones of a tourmaline crystal from a miarolitic pocket that vary significantly in their chemical composition lie perfectly on the straight line of a linear function. Therefore, such correlations seem to be independent of the chemical composition but dependent on the formation conditions. A high positive correlation seems to require equal formation conditions and an essentially closed system (see also [4]). The linear function of tourmaline from different pegmatites usually has different slopes. To develop a thermometer, tourmalines synthesized at 650 °C / 150 MPa [5] and at 750 °C / 200 MPa [6] were used for calibration. The resulting formula for the tourmaline thermometer is: $(1.249 - k) * 120 + 650 = T$ (°C), where k is the slope of the *X*-site charge to F function. Initial results deliver consistent results: 592 ± 50 °C for a tourmaline from a metapelite exposed to 630 ± 50 °C. The temperature of a tourmaline (schorl – fluor-elbaite series) from a miarolitic cavity [4] was calculated as 706 ± 50 °C. Although this value agrees with literature data (cited in [4]), it is not without controversy. The accuracy of this proposed tourmaline thermometer is currently limited due to calibration points at only two different temperatures.

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Acknowledgement

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THE SINGLE-DIFFUSION GEL GROWTH TECHNIQUE: A WAY OF PREPARING NOVEL METAL-ORGANIC COMPLEXES

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While countless metal-organic complexes can be obtained as a colloid or as fine-grained aggregates, their preparation in the form of single crystals remains a challenge. Unfortunately, it is often the precise determination of the compound's structure using its single crystal, which allows to ascertain its potential application in the chemical, environmental or pharmaceutic industry. A rather uncommon way of obtaining single crystals of metal-organic complexes is by means of the single-diffusion gel growth technique.

The structure of organometallic frameworks of indol-2- and indol-3-carboxylic acid (abbreviated as ICA2 and ICA3, respectively) with most $3d^{2+}$-transition metal cations is not known due to the above-mentioned lack of single-crystal material. Using the gel growth technique to sufficiently slow down the reaction rate (single-diffusion setup) in combination with enhancement of the solubility of the organic ligand (ICA2, ICA3) using a 1:1 H_2O/ethanol mixture as the supernatant solution, we were successful, for the first time, in preparing single crystals of both ICA2 and ICA3 copper salts and determine their structure. Furthermore, good-quality single-crystal individuals of novel ICA2 and ICA3 compounds of Zn, Co, Fe (to date ICA2 only) and Ni (to date ICA2 only) were obtained by the aforementioned technique, with the Zn-variants being known hydrates.

The use of 98% ethanol as the supernatant with the aim to dissolve as much ligand as possible in it leads, instead of obtaining the expected title compound, to the mere re-crystallization of the nearly saturated (and water-soluble) metal acetate in the gel due to dilution of H_2O by the inwards diffusing ethanol, reducing the solubility of the aqueous species.

Temperature (available range between 0°C – 78°C for this purpose, requiring silica gel for the 'high-temperature runs') does not seem to have any influence on the hydration state of the resulting compound. Still, in some cases as with Co, the use of 55°C contributes to better quality and size of the resulting metal-organic crystals.

Despite the single-diffusion gel growth technique being well-established [1], its combination with the concept of using two partly miscible or even immiscible fluids (here H_2O-based gel versus 50% ethanol to ensure solubility of all nutrients involved) can be considered as rather novel. Overall, this combination of two strategies, using the gel to sufficiently slow down the reaction rate while also employing two different liquids to ensure solubility of all nutrients involved, may present a stepping stone for the synthesis of many other metal-organic compounds in the form of single crystals.

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COORDINATION COMPOUNDS WITH INDOLE-2- AND INDOLE-3-CARBOXYLATES

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Indole-2- and indole-3-carboxylic acid (abbreviated as ICA2 and ICA3, respectively) and different metal-organic complexes of ICA2, ICA3 as well as their derivatives, have been studied in literature for different bioactive properties [1]. For example, Cu(II)-ICA2 was examined for its anticancer and anti-oxidant properties [2].

Using the single-diffusion gel growth technique (supernatant solution: ICA2/ICA3 in 1:1 H_2O/ethanol mixture, gel: metal acetate (0.2 M) was fixed in H_2O-based silica (≈ 0.3 M) gel) we synthesized single crystals of several novel compounds. We have prepared and structurally characterized the following ICA2/ICA3 complexes:

- $Cu_2(ICA3)_4(H2O)_2$,
- $Cu(ICA2)_2(H_2O)_2$,
- $[Ni(ICA2)_{4/2}(H_2O)_2]_n$,
- $[Co(ICA2)_{4/2}(H_2O)_2]_n$,
- $[Fe(ICA2)_{4/2}(H_2O)_2]_n$ and
- $[Na(ICA2)_{2/2}(H\text{-}ICA2)_{3/3}H_2O]_n$.

H-ICA2 stands for protonated indole-2-carboxylic acid.

Applying the gel growth technique, we further obtained two already known and published structures, Zn-ICA2 and Zn-ICA3 (CSD ref. codes PUBGID and KEYPAG, respectively). A short overview of the crystal structures and experimental results will be presented.

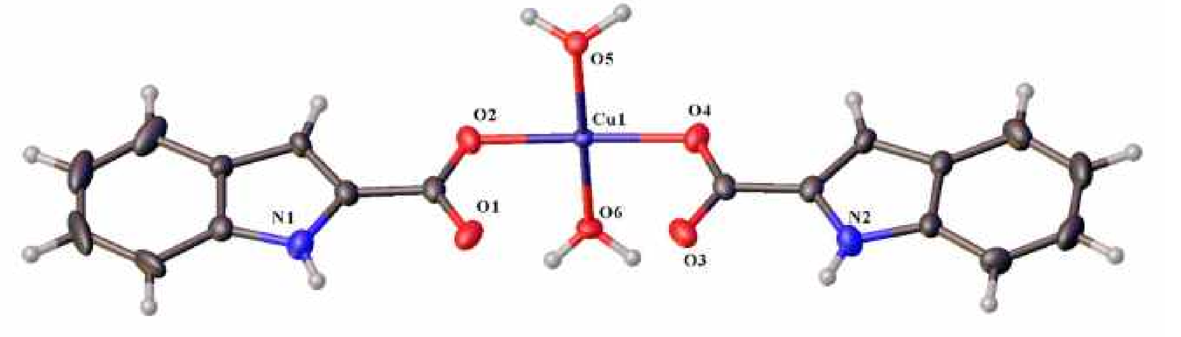

Figure 2. Picture of complex $Cu(ICA2)_2(H_2O)_2$.

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THE NEW CU(I)-CL- VOLUMINOUS ORGANIC POLYAMINE COMPOUNDS

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Four new **copper(I) -chloride** – **polyamine** compounds were discovered. 1,4-Diazabicyclo[2.2.2]octane (**dabco**), 1,6-diaminehexane (**hmda**) and 3,5-diamine-1,2,4-triazole (**datrz**) were used as polyamine ligands. A search of CSD CCDC [1] revealed some coordination compounds with these ligands [2-5]. It should be noted that only a few ratios of reagents were used in the synthetic work. This was a reason for the systematic investigation of these systems on the basis of the composition space diagram.
The two **dabco** derivatives and the **H_2hmda** salt were obtained by electrochemical reaction**$Cu^{2+}+Cu^0=2Cu^+$** in ethanol. A compound with **datrz** was also synthesized by **$Cu^{2+}+Cu^0=2Cu^+$** reaction under **solvothermal conditions**.

The compound **(Hdabco)Cu_2Cl_3** contains a monoprotonated **$Hdabco^+$** cation, which is coordinated to the **Cu1** ion *via* an unprotonated **N1**. Both crystallographically independent copper centers are three-coordinated. Due to the bridging function of the chloride ligand, infinite cuprochloride chains running along the b-axis appear.

The crystal structure of the compound **Cu_2Cl_2(Dabco)** contains a neutral **dabco** ligand that serves as a bridge between two copper centers. Each metal ion is coordinated by a nitrogen atom of **dabco** and two bridging chlorine ions. The inorganic part of the structure is represented as infinite **$(CuCl)_n$** chains.

The crystal structure of the compound **$[H_2hmda]^{2+}[Cu_2Cl_4]^{2-}$** contains infinite $[(CuCl_2)^-]_n$ chains, which occur due to the bridging function of the chlorine centers. The two amine groups of hmda are protonated, and **H_2hmda^{2+}** dications connect inorganic chains via hydrogen bonds. The crystallographically independent part contains the **$CuCl_2^-$** unit and a half of the organic dication.

The crystal structure of the compound **CuCl(datrz)** contains a neutral **datrz** ligand that acts as a bridge between two copper centres, resulting in infinite (**$Cu(datrz)_n$**) chains. Each copper centre is coordinated by two nitrogen atoms of different **datrz** ligands and a terminal chloride ligand. Each chlorine atom forms a hydrogen bond with the amino group of the same chain and with the NH group of the heterocycle ring of the neighbouring chain.

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SYNTHESIS AND STRUCTURE OF CU(I) COMPLEX WITH SCHIFF BASE OF AMINOGUANIDINE AND 2-(DIPHENYLPHOSPHINO)BENZALDEHYDE

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From the warm methanol solutions of 2-(diphenylphosphino)benzaldehyde-aminoguanidine and copper(II) nitrate, in a 1:1 molar ratio, yellow single crystals of the copper(I) complex of the formula $[Cu_2(HL)_2(\mu\text{-}Cl)(\mu\text{-}NO_3)ClX]$, where X = Cl, NO_3 (Figure 1), were yielded. The structural confirmation was achieved through SC-XRD analysis, corroborated by PXRD studies. The coordination of the Schiff base was established through the phosphorus atom, which is not surprising since the reduction of copper(II) to copper(I) took place. However, it is rather unusual for the Schiff bases of aminoguanidine to act as monodentate ligands. Apart from the Schiff base, the coordination sphere contains one chlorido and one nitrito bridge connecting two copper centers, forming one six-membered metallocycle. One of the terminal coordination sites is occupied by chlorido ligand, while at the other one chlorido and nitrito anions are interchanged. This coordination mode makes both copper centers situated in a deformed tetrahedral environment. These results give novel insight into examining structural changes of aminoguanidine Schiff bases due to different modes of coordination and protonation, thus enabling the knowledge of structure-properties relationship and design of novel materials with different features.

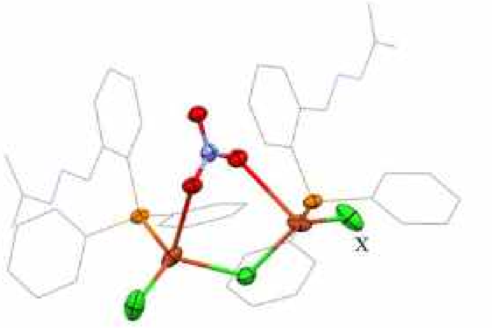

Figure 1. Molecular structure of $[Cu_2(HL)_2(\mu\text{-}Cl)(\mu\text{-}NO_3)ClX]$, X = Cl, NO_3

Crystallographic data: monoclinic crystal system, $I2/a$, a = 19.3390(12), b = 8.6966(5), c = 24.5077(15) Å, β = 94.920(6) °, V = 4106.6(4) Å^3, Z = 4. Refinement based on $F2$ (329 parameters): $R1$ = 0.048, $wR2$ = 0.135, S = 1.07, for all data, and $R1$ = 0.032 for 4073 reflections with $I \geq 2\sigma(I)$.

Acknowledgement
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REACTIVITY OF CYANOGEN TOWARDS [XeF]$^+$ CATION

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The presence of σ-hole on the polarized xenon atom in certain xenon(II) species such as the [XeF]$^+$ cation allows the coordination of *N*-donor Lewis bases and thus the facile formation of xenon–nitrogen bonds in solution and in the solid state [1−3]. However, the possibility of bonding two or more xenon(II)-based Lewis acids to the same polytopic nitrogen base has not been explored, although such bases have been used [2].

To investigate this possibility, we reacted cyanogen (NCCN), a simplest ditopic nitrogen base, with [XeF][AsF$_6$] in anhydrous HF at low temperatures. This resulted in crystallization of the [FXeNCCNXeF][AsF$_6$]$_2$ salt. The novel cation is the first example of a nitrogen base that is *bis*-coordinated with [XeF]$^+$ cations and features the longest Xe−N and the shortest Xe−F bonds in the series of nitrile–XeF$^+$ adduct cations [2]. The [FXeNCCNXeF][AsF$_6$]$_2$ salt undergoes rearrangement at room temperature by a formal fluoride shift from xenon to carbon and converts to [XeNC(F)C(F)NXe][AsF$_6$]$_2$ salt, which is the first example of a C=N−Xe$^{\mathrm{II}}$ bonding modality. Due to the surprising stability of this compound at room temperature and the presence of a strongly polarized Xe$^{\mathrm{II}}$ atom with a pronounced σ-hole in the cation it can be used as a suitable reagent to study the reactivity of this novel N−Xe$^{\mathrm{II}}$ moiety towards Lewis bases. This was demonstrated by the low-temperature synthesis and crystallization of the [CH$_3$CN···XeNC(F)C(F)NXe···NCCH$_3$][AsF$_6$]$_2$ adduct cation salt (Figure 1), which is the second example of a crystallographically characterized compound with N−Xe$^{\mathrm{II}}$−N linkage [4].

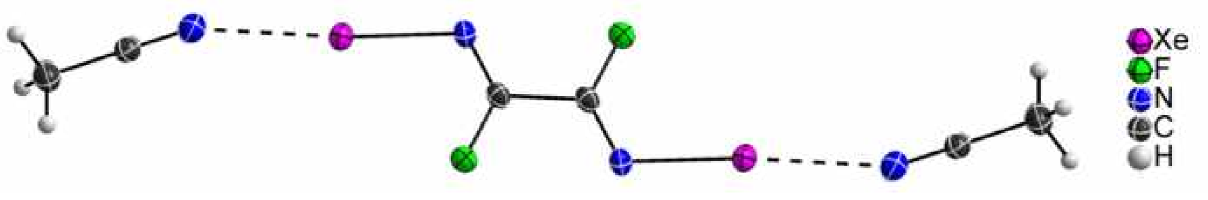

Figure 1. The crystal structure of [CH$_3$CN···XeNC(F)C(F)NXe···NCCH$_3$]$^{2+}$ adduct cation. Thermal ellipsoids are shown at the 50% probability level, whereas the hydrogen atoms are represented as spheres of arbitrary radius.

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COORDINATION OF CARBAMOYL FLUORIDE TO FLUORIDOXENON(1+) CATION

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In a large majority of xenon(II) compounds, the noble-gas atom is typically only bonded to fluorine atoms. The salts of the Lewis acidic cation $[XeF]^+$ can serve as versatile precursors for synthesizing compounds where oxygen or nitrogen are bonded to xenon through reactions with suitable donor ligands acting as Lewis bases. One of the main limitations for donor ligands to be suitable for reactions with $[XeF]^+$ is the requirement of a relatively high ionization potential (>10.9 eV) in order to withstand the strongly oxidizing nature of $[XeF]^+$ [1]. In the absence of experimental data, the ionization potential can be accurately calculated using density functional theory (DFT) methods [2].

So far only a handful of oxygen donor ligands have been explored (Fig. 1, left) [3–6], and only the fluorosulfate derivative $[FSO_3-(XeF)_2]^+$ has been characterized crystallographically [4]. In this work, carbamoyl fluoride (H_2NCOF) was studied as the potential oxygen donor ligand for the synthesis of Xe−O-bonded compound. An initial evaluation of its vertical ionization potential by DFT (11.4 eV) confirmed that it should not be oxidized by $[XeF]^+$. A low-temperature reaction of H_2NCOF with $[XeF][AsF_6]$ in anhydrous HF afforded the $[H_2NC(F)O-XeF][AsF_6]$ adduct cation salt. The novel compound is stable only at low temperatures, therefore, low-temperature techniques for crystallization and single-crystal X-ray diffraction were used to determine its crystal structure (Fig. 1, right). The product was also characterized by low-temperature Raman spectroscopy and studied by quantum-chemical calculations.

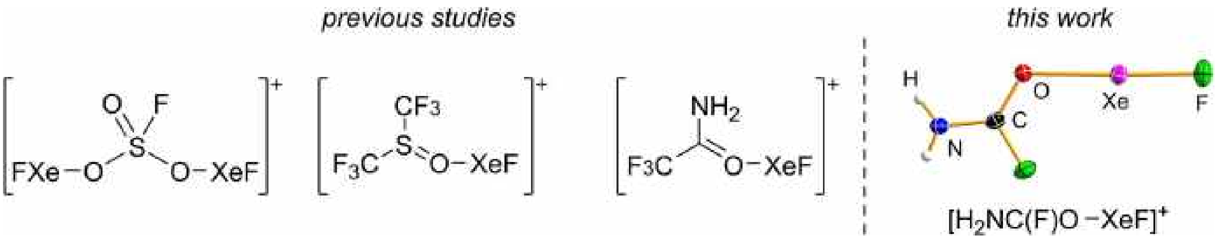

Figure 1. The known XeF^+ adduct cations with O-donor Lewis bases

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(E)-N'-((5-(HYDROXYMETHYL)FURAN-2-YL)METHYLENE) BENZOHYDRAZIDE AND ITS COPPER(II) COMPLEX: SYNTHESIS AND CRYSTAL STRUCTURE

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The title compound, H_2L, synthesized from 5-hydroxymethylfurfural and benzohydrazide, belongs to N-acylhydrazone class of organic ligands, as well as its bis-chelate copper(II) complex, were synthesized for the first time. Recently, relative compounds have attracted increasing interest due to their various and valuable properties - physical, chemical, and biological, that affords to consider them as candidates for the creation of modern optical and magnetic materials, biosensors, catalysts, and medicines [1-3].

The crystal structures of H_2L and $[Cu(HL)_2]$ were determined by single crystal X-ray diffraction analysis. The key role of hydrogen bonds in the formation of their crystal lattices was revealed. The compound $[Cu(HL)_2]$ crystallizes in two polymorphic modifications with the following parameters: (A) triclinic, *P 1 (№ 2)*, a=9.077(6) Å , b=11.115(8) Å, c=12.861(7) Å, α=81.810(5)°, β=78.985(5)°, γ=71.427(6)°, V=1202.62(14) $Å^3$ at 150 K, and (B) monoclinic, *$P\ 2_1/c$ (№ 14),* a=14.474(4) Å, b=17.286(4) Å, c=10.504(3) Å, β=109.636(3)°, V=2475.20(12) $Å^3$ at 150 K (Fig.).

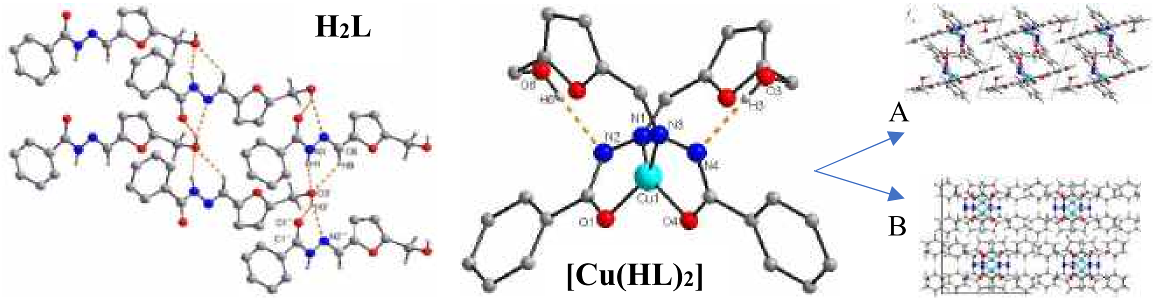

Figure 1. Crystal structure of H_2L, metal coordination in $[Cu(HL)_2]$ and its two polymorphs A and B (packing is projected along direction *c*)

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DIVERSITY OF MIXED CUPRO(I)-CYANO-THIOCYANATO ANIONIC POLYMERS

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The application of our recently developed synthetic approaches has led to a variety of novel anionic cupro(I)-cyano-thiocyanato frameworks. One of them, $\{[Cu_8(CN)_6(SCN)_4]^{2-}\}_n$, has a 3D architecture with infinite channels filled with solvated M2+ cations and was obtained by direct interaction of CuCN and CuSCN with the corresponding transition metal salt in an appropriate solvent. Another original synthetic approach allowed the preparation of the three-dimensional anionic framework $\{[Cu_4(CN)(SCN)_6]^{3-}\}_n$ based on solvated lanthanide M^{3+} cations as counterions. The compounds with two-dimensional polymeric anions $\{[Cu_5(CN)_5(SCN)_3]^{3-}\}$, $\{[Cu_4(CN)_5(SCN)_2]^{3-}\}$ and $\{[Cu_2(CN)(SCN)_2]^{-}\}$ were also synthesized. It is noteworthy that our synthesis methods did not lead to any of the already known cupro(I)-cyanato coordination polymers.

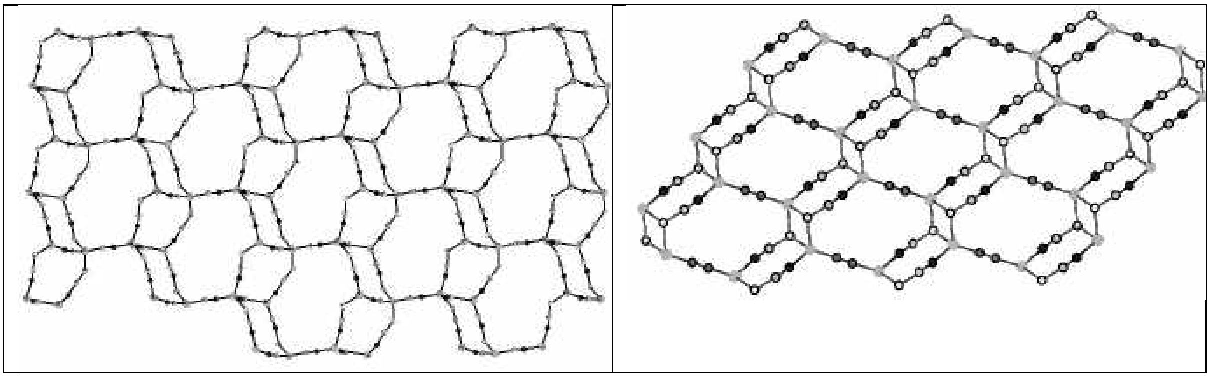

Figure 1. Two-dimensional polymeric anions $\{[Cu_4(CN)_5(SCN)_2]^{3-}\}_n$ (left) and $\{[Cu_2(CN)(SCN)_2]^{-}\}_n$ (right).

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COORDINATION COMPOUNDS WITH 5-SULFOSALICYLATES

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Three novel coordination compounds with 5-sulfosalicylic acid (H_3L) anion were synthesized and characterized. These are $\{[Cu(inia)(HL)(H_2O)_2](H_2O)_2\}_n$ **1**, $[Zn(inia)_2(HL)(H_2O)_2](H_2O)$ **2** and $\{(CH_6N_3)_2[Cu(L)(H_2O)]_2(2OHpy)_4\}$ **3** (inia – isonicotinamide $C_6H_6N_2O$; 2OHpy – 2-hydroxypyridine C_5H_5NO).

The title main ligand, with three possible coordination sites, enables a variety of coordination possibilities from monomeric to polymeric. A check of the structural survey within CSD [1] reveals several hits, among which Cu, Zn and Cr compounds are seen [2-4].

A polymeric compound **1** shows the octahedral equatorial coordination plane, being composed by two water and one inia molecules, along with a monodentate HL carboxylate group. The two axial positions of the Jahn-Teller distorted octahedron are filled by two oxygen atoms of two sulfonate moieties in CuO_3NO_2.

On the other hand, a mononuclear Zn compound **2** has two inia molecules along with two coordinated water molecules. With one carboxylate oxygen atom they all form a square pyramidal coordination sphere around central Zn(II). The second carboxylate oxygen atom is at the other axial position, potentially completing significantly distorted coordination octahedron ZnO_3NON. A protonated hydroxyl group in **1** and **2** enables strong intramolecular O–H···O bonds in these two compounds.

Differently to **1** and **2**, the third compound **3** contains a binuclear Cu(II) complex anion, where fully deprotonated L is present. Also herein, the octahedral coordination sphere is found however one carboxylate oxygen atom of each L in $[Cu(L)(H_2O)]_2$ is bridging the two Cu(II) ions. Because these bridging atoms form the basal square plane of the J-T Cu(II) octahedron, a strong magnetic coupling is expected among the two metal centers. The CuO_4O_2 coordination basal square is completed by the hydroxyl and the water O atoms, while the axial positions are occupied by the sulfonate O atoms. Outside the coordination moiety, the guanidinium cations as well as the 2OHpy molecules are seen. All forming a net with H-bonds and π–π stackings.

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ON THE SYNTHESIS AND STRUCTURE OF SALTS CONTAINING THE PECULIAR $[M^{IV}F_3(XeF_2)_3]^+$ (M = Pd, Pt) CATIONS

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In 1962, the reactivity of the noble gases, hitherto considered inert, was demonstrated by Neil Bartlett's landmark synthesis of $XePtF_6$ [1]. Subsequent investigations revealed that the compound was most likely an $XeF_2{\cdot}PtF_4$ adduct [2], which led to the exploration of analogous XeF_2–MF_4 systems. Only four crystal structures of such adducts have been reported to date and they are characterised by polyfluoridometallate(IV) backbones formed by fluoride-bridged $[MF_6]$ octahedra [3–5]. In the present work, reactions in anhydrous HF solutions containing $[M^{IV}F_6]^{2-}$ and $[AsF_6]^-$ anions were explored, resulting in the isolation of single crystals of $[Xe_2F_3][MF_3(XeF_2)_3][AsF_6]_2$ (M = Pd, Pt) (Fig. 1), whose structures were determined by low-temperature single-crystal X-ray diffraction. The $[MF_3(XeF_2)_3]^+$ cations are an unprecedented species, as they represent the first examples of XeF_2-coordinated metal(IV) mononuclear species, as well as the first case of more than one XeF_2 molecule coordinating to an M^{IV} centre. The arrangement of the fluorine atoms coordinating the M^{IV} is slightly distorted octahedral, with three of the fluorine atoms donated by the XeF_2 molecules forming *fac* arrangement. In addition, the compounds were investigated by low-temperature Raman spectroscopy, and quantum-chemical calculations were performed in order to obtain the optimised gas-phase geometries of the cations and to assess the extent of XeF_2 ionisation.

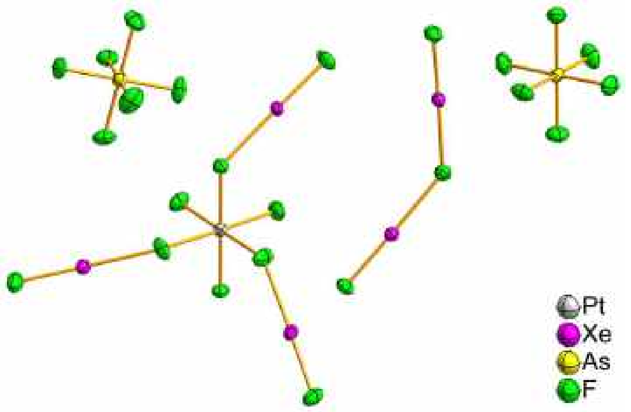

Figure 1. Crystal structure of $[Xe_2F_3][PtF_3(XeF_2)_3][AsF_6]_2$ (50% probability ellipsoids).

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SYNTHESIS AND STRUCTURAL ANALYSIS OF NOVEL Xe^{II}–N-BONDED COMPOUNDS

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The FXe–N-bonded adduct cations have been synthesized with only a small selection of nitriles RCN and fluorinated heterocycles [1–4]. The driving force for the formation of such compounds is the donation of a lone electron pair of nitrogen to the σ-hole of the Xe^{II} atom [1]. However, there are no reports of multiply bonded $[XeF]^+$ cations to the same polytopic Lewis base, which raises the question of whether such species could exist.

In this work, malononitrile ($NCCH_2CN$) was investigated as a possible ditopic donor by reactions with $[XeF][AsF_6]$ in anhydrous HF at low temperature. Two adducts, $[NCCH_2CN–XeF][AsF_6]$ and $[NCCH_2CN–XeF][AsF_6]·HF$, were isolated and structurally characterized (Figure 1). In crystal structure of the first compound the Xe–N bond distance is equal to 2.175(6) Å and the second cyano group is involved in a rather long hydrogen bond with the CH_2 moiety [*d*(N···C) = 3.17(1) Å] of the neighbouring adduct cation. Whereas in the HF solvate, a slightly longer Xe–N bond distance of 2.2116(18) Å is observed, and the second cyano group is hydrogen bonded to the cocrystallized HF molecule [*d*(N···F) = 2.620(1) Å, ∡(N···H–F) = 169.95(1)°].

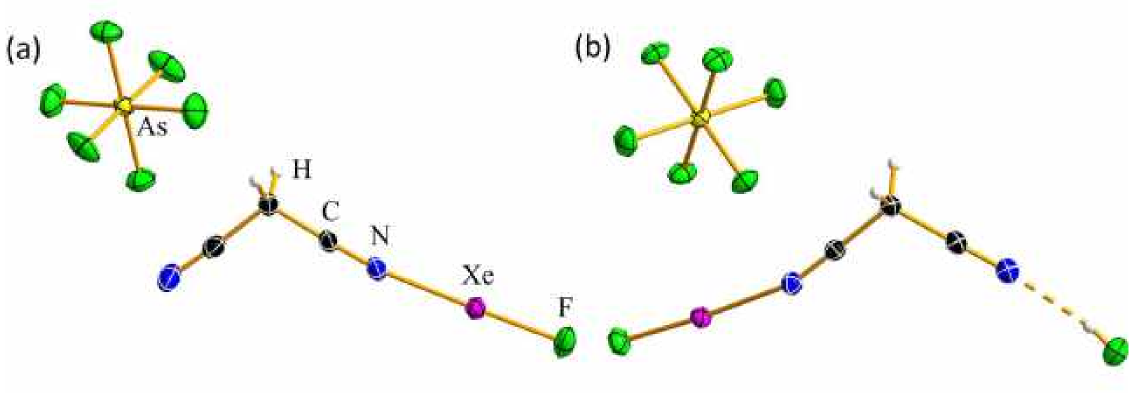

Figure 1. The crystal structure of (a) $[NCCH_2CN–XeF][AsF_6]$ and (b) $[NCCH_2CN–XeF][AsF_6]·HF$. Thermal ellipsoids are depicted at the 50% probability level.

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SYNTHESIS, CHARACTERIZATION AND GAS SENSING PROPERTIES OF PLATINUM NANOPARTICLES DISPERSED ON IRON OXIDE SUPPORT

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The $Pt/\alpha\text{-}Fe_2O_3$ samples (FP samples) with platinum loadings between 1 and 10 mol% were mechanochemically synthesized in spherical morphology starting from $\alpha\text{-}Fe_2O_3$ (hematite) powder obtained from iron(II) acetate and from platinum(II) acetylacetonate dissolved in toluene. The hematite structure was confirmed by Mössbauer and Raman spectroscopy. Atomic resolution scanning transmission electron microscopy (AR STEM) showed that the platinum was uniformly dispersed on the $\alpha\text{-}Fe_2O_3$ in the form of small platinum nanoparticles. The XRD results showed that the FP samples were entirely composed of $\alpha\text{-}Fe_2O_3$ (hematite), but the platinum maxima were not found in any XRD pattern, even at the highest platinum loading of 10 mol% (sample FP-10). The unit cell parameter values of hematite in the FP samples did not change with Pt loading, confirming that there was no substitution of Fe^{3+} for Pt^{4+} in hematite. The Pt-4f-XPS results showed that the dispersed platinum on $\alpha\text{-}Fe_2O_3$ supports consisted of all three oxidation states of platinum: Pt^{4+}, Pt^{2+} and Pt^0 [1, 2]. The gas sensing properties of the samples were measured by depositing $Pt/\alpha\text{-}Fe_2O_3$ suspensions on glass substrates with interdigitated gold electrodes using the drop-casting technique [3]. The changes in the electrical resistance of the samples upon exposure to H_2 gas were measured at different temperatures from 293 K to 553 K. We found that the samples with Pt were sensitive to H_2, but no dependence of sensitivity on Pt loading was observed. While our samples already responded at room temperature, their sensitivity and response time improved significantly at higher temperatures.

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CRYSTAL STRUCTURES OF NOVEL COPPER COORDINATION COMPOUNDS WITH PYRIDINECARBONITRILES

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Pyridinecarbonitriles (pcn), often also referred to as cyanopyridines, are promising ligands for the formation of pyridine-containing coordination polymers, as they contain two different N-donor atoms, which enable them to act as interlinking ligands [1]. Coordination compounds containing pcn derivatives are under investigation due to their possible use as antiparasitic drugs [2] and in cancer treatment [3].

The preparation and characterization of novel copper coordination compounds with 2-, 3-, and 4-pcn are reported. Compound **1** with the formula $[\mathrm{Cu_2}(\mu\text{-Ac})_4(3\text{-pcn})_2]$ forms a *paddle-wheel* structure with four bridging acetate ions and two 3-pcn ligands coordinated *via* the ring nitrogen. The asymmetric unit of product **2** with the formula $[\mathrm{Cu(NO_3)_2(CH_3CN)}(4\text{-pcn})_2]\cdot\mathrm{CH_3CN}$ is characterized by a 5+2-coordinated Cu(II) ion surrounded by two chelating nitrate ions, two 4-pcn ligands coordinated *via* the ring nitrogen and one coordinated molecule of the solvent. In the reaction between copper nitrate and 2-pcn in water under reflux, 2-pcn undergoes hydrolysis to picolinamide (pic), forming compound **3** with two chelating pic ligands coordinated to copper *via* the ring nitrogen and the oxygen of the carboxamide group. All of the products were further characterized by FTIR, thermal analysis (including the identification of final products after thermal decomposition by pXRD) and magnetic measurements.

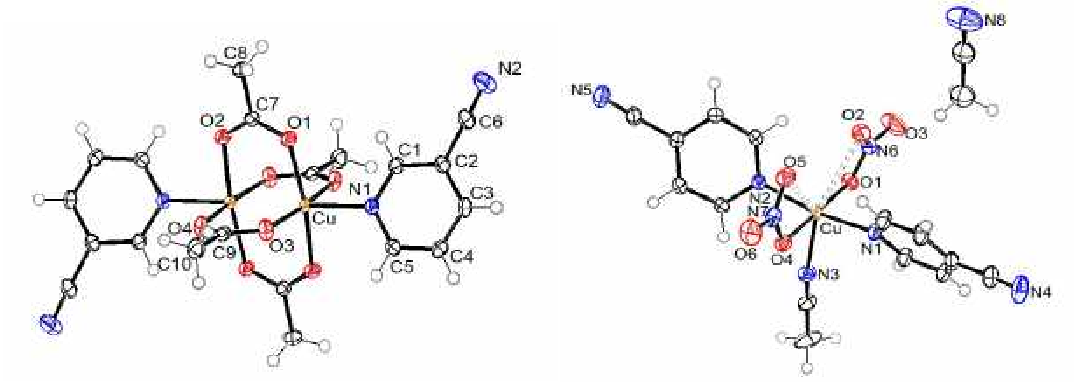

Figure 1. ORTEP drawings of coordination compounds **1** and **2** with labelling of non C, H atoms.

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ZINC COMPLEXES WITH DERIVATIVES OF PICOLINIC ACID

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Diabetes mellitus is a chronic disease experiencing a significant rise in prevalence during the 21st century. Recent research suggests that various metal ions, including Cr, Mn, Mo, W, V, and Zn, possess anti-diabetic properties. Among these, zinc holds particular importance for human health. It plays a crucial role in DNA synthesis, cell growth, protein formation, tissue repair, and immune system function [1]. Notably, Zn also influences insulin storage and promotes the secretion of glucose transporter type 4 (GLUT-4), making it a prime target for anti-diabetic drug development. Studies have revealed that the form of zinc entering the human body significantly impacts its efficacy. Complexation with ligands offers a promising strategy to enhance its effectiveness in anti-diabetic assays. Coordination compounds offer several advantages over their inorganic counterparts. These advantages include the ability to fine-tune biological activity, improve stability against degradation before absorption, enhance targeting specificity, and mitigate potential toxicity. Previously, zinc complexes with picolinic acid (pyridine-2-carboxylic acid) and its derivatives have demonstrated promising insulin-mimetic activity [2]. Based on these findings, our research has been extended to explore the potential of dipicolinic acid (pyridine-2,6-dicarboxylic acid) and its derivatives as ligands.

We have successfully synthesized Zn(II) complexes with various picolinic acid derivatives using zinc chloride, zinc acetate, and zinc sulfate as zinc sources. The ligands primarily bind to the central metal ion in a multidentate fashion.

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RECENT ADVANCES IN COORDINATION CHEMISTRY OF METAL COMPLEXES WITH XeF_2 AS A LIGAND

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By reacting metal fluorides with strong Lewis acids (such as AsF_5, SbF_5, BiF_5) in anhydrous HF (aHF), metal salts of weakly coordinating anions are obtained. These anions make specific metal centres available for coordination with weaker fluorido ligands, such as xenon difluoride (XeF_2), where a diverse array of metal complexes, represented by the general formula $[M^{n+}(XeF_2)_m(AF_6^-)_n]$, has been synthesized and structurally characterized [1].

In this work, the wide structural diversity and varied coordination modes of XeF_2 observed in the aforementioned complexes will be described, showcasing specific examples from our recent research. Expanding the isostructural family $[Ba(XeF_2)_4(AF_6)_2]\cdot XeF_2$ (where A = As, Sb, V, Nb, Ru) [1–4], a novel member $[Ba(XeF_2)_4(TaF_6)_2]\cdot XeF_2$ has been added to this series. Additionally, Zn^{2+} in a homoleptic environment of six XeF_2 ligands was found in $[Zn(XeF_2)_6(AsF_6)_2]$ (Figure). In another instance, the bridging bonding modality of XeF_2 observed in the crystal structure of $[Nd(XeF_2)_3(TaF_5)_3]$ results in the formation of channels along the c-crystallographic axis.

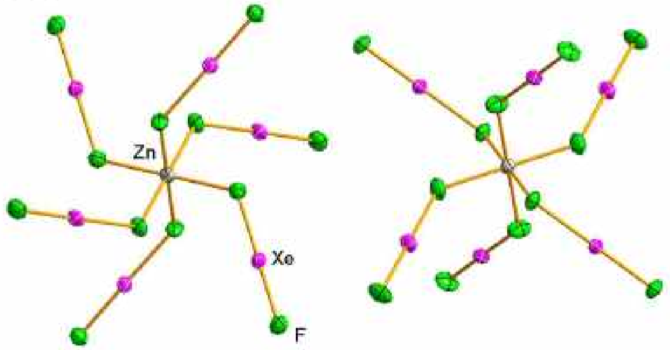

Figure 1. Two crystallographically independent homoleptic $[Zn(XeF_2)_6]^{2+}$ cations were observed in the crystal structure of $[Zn(XeF_2)_6(AsF_6)_2]$ (50% probability ellipsoids).

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STRUCTURE-PROPERTY REATIONSHIP IN MECHANOFLEXIBLE CRYSTALLINE COORDINATION POLYMERS

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In contrast to their generally accepted inflexible properties, molecular crystals may, under certain circumstances, also adapt to various external stimuli whilst maintaining their integrity [1]. Being enriched with adaptable properties, crystals are becoming exceptional candidates for application in advanced technologies where they bring in a range of fine-tunable properties. However, the practical application and implementation of mechanoflexible crystalline materials in smart devices and future technologies necessitate not only excellent materials' performances but also highly and precisely controllable mechanical outputs. To achieve that, an in-depth understanding of structural prerequisites and consequences of mechano-flexibility and their well-defined correlation with mechanical properties is required.

Coordination polymers (CP), in particular their 1-D subgroup, emerged as an ideal class of crystalline materials that allows exploring the structural background and underlying principles leading to targeted flexible outputs as well as their structure-property relationship [2–5]. Here, we present a new family of 1-D isostructural Cd(II) coordination polymers equipped with the moiety that allows extensive structural and mechanical characterisation as well as quantification. Crystal mobilities observed on the macroscopic scale are correlated with structural features and mobilities on a molecular level, while a correlation with relevant 1-D CP families has also been drawn. Extensive experimental findings were additionally complemented by computational efforts [6].

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CSD WORKSHOP: UNLOCKING NEW INSIGHTS THANKS TO OVER A MILLION STRUCTURES

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The Cambridge Structural Database (CSD) contains a wealth of information that can be used to derive new knowledge. You can use this resource to extract invaluable insights from the over one million crystal structures, informing and accelerating your research and development.

In this hands-on session we will introduce you to functionality from the CSD Portfolio to help you perform sophisticated analysis and prediction of molecular geometry, intermolecular interactions, and assist with advanced visualisation. You will learn more about solid state analysis and about how tools in Mercury can enable you to leverage the wealth of data in the CSD to provide insight into structural features and intermolecular interactions that are important to structural stability and mechanical properties. Along the way you will learn some tips and tricks for visualization and analysis with our software Mercury.

This will be a hands-on interactive session where there will be presentations, demonstrations and you will get the opportunity to use the software with hands-on exercises. Participants are encouraged to bring their own laptops and a temporary licence for the CSD package will be provided if necessary.

This workshop will be open to all levels of expertise with the CSD: we will cover the basics for new users of the CSD and we will also cover new functionality and tips and tricks for experienced users and attendees who joined the workshop last year.

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A global leader in providing anti-infective treatments and other critical care therapies for serious and often life-threatening conditions

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Headquartered in Copenhagen, Denmark and owned by Novo Holdings A/S, Xellia Pharmaceuticals has more than 1800 employees globally. From state-of-the-art manufacturing sites in the U.S., China, Denmark and Hungary to R&D sites in Norway and Croatia and commercial operations across Europe, Asia, the Middle East and North America; Xellia Pharmaceuticals' strong market position is built on more than 120 years of pharmaceutical industry experience. With the patient in focus, Xellia is building a pipeline of value-added critical care therapies which aim to enhance patient care by providing convenience and ease of use for healthcare professionals.

Further information about Xellia can be found at: **www.xellia.com**

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oxford diffraction
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Selvita

Selvita: Integrated Drug Discovery partner of choice

Having experience in both **pharma and biotech R&D,** we are well aware of what it means to discover a hit and transform it into a drug. You can best benefit from this "insider" experience through our integrated drug discovery services.

TARGET VALIDATION

- Target validation with genetic and pharmacological approach
- Biomarker expression and post-tranlational modifications
- Cellular processes

HIT IDENTIFICATION

- Assay development and screening
- HTS/vHTS/HCS
- Priopietary macrocycle library
- Fragment-based drug design
- Structure- and ligand-based drug design
- Biophysical methods

HIT TO LEAD AND LEAD OPTIMIZATION

- Medicinal and synthetic chemistry
- CADD
- In vitro pharmacology
- ADME/DMPK
- Protein production an X-ray crystallography
- Early toxicology
- In vivo pharmacology
- Translational research

PRECLINICAL/CLINICAL CANDIDADE

- Non-GLP tox studies
- Solid state
- GLP bioanalysis
- Ex vivo analysis for biomarker research
- Batch release for clinical trials (GMP)

Foundations of our excellence:

- ✓ Extensive experience in drug discovery from target validation to preclinical development
- ✓ Dedicated IDD Department overseeing all IDD projects and comprising of experienced scientists with a > 20-year track record from leading biotech and pharma companies
- ✓ Therapeutic area expertise, primarily in inflammation, infection, oncology, and fibrosis
- ✓ Increasing use of AI algorithms across all business areas with particular emphasis on chemistry and biology
- ✓ Medicinal chemistry and strong skills in organic synthesis
- ✓ Multidisciplinary teams of high-performing scientists and experienced logistics team
- ✓ Strong emphasis on translational science

Visit our website
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CROATIAN CRYSTALLOGRAPHIC ASSOCIATION

SLOVENIAN CRYSTALLOGRAPHIC SOCIETY

THE 30TH CROATIAN-SLOVENIAN CRYSTALLOGRAPHIC MEETING

Veli Lošinj, Croatia

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