HRVATSKA AKADEMIJA ZNANOSTI I UMJETNOSTI
RAZRED ZA MATEMATIČKE, FIZIČKE I KEMIJSKE ZNANOSTI

ZNANSTVENO VIJEĆE ZA KRISTALOGRAFIJU HAZU –

HRVATSKA KRISTALOGRAFSKA ZAJEDNICA

DVADESET PETA OBLJETNICA OSNUTKA ZNANSTVENOGA VIJEĆA ZA KRISTALOGRAFIJU HAZU – HRVATSKE KRISTALOGRAFSKE ZAJEDNICE

SAŽETCI PRIOPĆENJA NA SEMINARU SUVREMENA KRISTALOGRAFIJA U HRVATSKOJ POREČ 2017.

ZAGREB, 2017.

HRVATSKA AKADEMIJA ZNANOSTI I UMJETNOSTI
RAZRED ZA MATEMATIČKE, FIZIČKE I KEMIJSKE ZNANOSTI

ZNANSTVENO VIJEĆE ZA KRISTALOGRAFIJU HAZU –
HRVATSKA KRISTALOGRAFSKA ZAJEDNICA

HRVATSKA AKADEMIJA ZNANOSTI I UMJETNOSTI
RAZRED ZA MATEMATIČKE, FIZIČKE I KEMIJSKE ZNANOSTI
ZNANSTVENO VIJEĆE ZA KRISTALOGRAFIJU HAZU –
HRVATSKA KRISTALOGRAFSKA ZAJEDNICA

DVADESET PETA OBLJETNICA OSNUTKA ZNANSTVENOGA VIJEĆA ZA KRISTALOGRAFIJU HAZU – HRVATSKE KRISTALOGRAFSKE ZAJEDNICE

SAŽETCI PRIOPĆENJA NA SEMINARU SUVREMENA KRISTALOGRAFIJA U HRVATSKOJ POREČ 2017.

ZAGREB, 2017.

PREDGOVOR

Znanstveno vijeće za kristalografiju HAZU – Hrvatska kristalografska zajednica (*HKZ*) obilježava ove godine dvadeset petu obljetnicu osnivanja. Međutim, već 1966. Predsjedništvo (tadašnje) *Jugoslavenske akademije znanosti i umjetnosti* osnovalo je *Jugoslavenski centar za kristalografiju* pri *Razredu za matematičke*, *fizičke i tehničke znanosti*, kao naučni savjet sa zadatkom promicanja kristalografije i njene primjene u znanosti i tehnici. *Centar* je djelovao do 1991. te priređivao redovite godišnje znanstvene skupove s međunarodnim sudjelovanjem, priredio je šest skupova u suradnji s kristalografima Italije, te *13th European Crystallographic Meeting*, *ECM13*, u Ljubljani-Trstu 1991. *Centar* je objavljivao *Godišnjak* (*Annual*, u izdanju *JAZU*) koji je sadržavao priopćenja podnesena na skupovima te važne informacije o znanstvenoj djelatnosti svojih članova.

Po uspostavi Republike Hrvatske, Predsjedništvo *Hrvatske akademije znanosti i umjetnosti* osnovalo je 28. veljače 1992. *HKZ* kao sljednicu *Centra*, u okviru *Razreda za matematičke, fizičke i kemijske znanosti*.

HKZ je interdisciplinarna udruga, koja okuplja kemičare, fizičare, biologe, mineraloge, geologe, farmaceute, metalurge i druge znanstvenike, te broji oko 120 znanstvenika, znanstvenih novaka i studenata. Od svojeg osnivanja punopravna je i aktivna članica *Europske kristalografske zajednice* (*European Crystallographic Association*, *ECA*) i *Međunarodne kristalografske unije* (*International Union of Crystallography*, *IUCr*). O djelatnostima *HKZ*-a redovito se objavljuju prikazi u glasilima međunarodnih udruga *IUCr Newsletter* i *ECA e-Newsletter*. U glasilu *IUCr Newsletter* objavljen je 2011. opširni prikaz *Crystallography in Croatia* (prvi od prikaza za 14 država jugoistočne Europe).

Od svog osnutka, *HKZ* priređuje, u suradnji sa *Slovenskim kristalografskim društvom*, redovite godišnje znanstvene skupove s međunarodnim sudjelovanjem naizmjence u Hrvatskoj i u Sloveniji. Posljednja dva sastanka bila su: 24*th Croatian-Slovenian Crystallographic Meeting* (*CSCM24*), održan u Bolu od 21. do 25. rujna 2016; *25th Slovenian-Croatian Crystallographic Meeting* (*SCCM25*) održan u Ljubljani od 14. do 18. lipnja 2017.

Savjet *ECA* povjerio je 2011. hrvatskim kristalografima priređivanje *29th European Crystallographic Meeting* (*ECM29*) koji je održan u Rovinju od 23. do 28. kolovoza 2015. i na kojemu je bilo 1050 sudionika. Početne pripreme za *ECM29* obavio je Odbor *HKZ*-a i imenovao *Odbor za pripremu skupa*; taj *Odbor* prerastao je u *Hrvatsku udrugu kristalografa*, koja je preuzela i vrlo uspješno provela sve aktivnosti glede priprema *ECM29*, uz suglasnost Skupštine *HKZ*-a (27. rujna 2012.).

Tijekom prethodnih pedeset skupova (ne uključujući *ECM13* i *ECM29*), od 1966. do 2017., podneseno je oko 250 pozvanih predavanja i oko 3000 kratkih priopćenja. Teme pozvanih predavanja i kratkih priopćenja podnesenih na tim skupovima odnose se na suvremeni razvoj kristalografije i bliskih znanstvenih područja, kao molekulske biologije, fizike i kemije čvrstoga stanja, znanosti o materijalima, farmakologije, mineralogije.

Skupovi hrvatskih kristalografa imaju veliki odjek u međunarodnim kristalografskim i znanstvenim udrugama. Izvješća o prethodnim znanstvenim skupovima kristalografa Hrvatske i Slovenije objavljena su u glasilu *IUCr Newsletter*. Sve to potvrđuje izrazitu prepoznatljivost kristalografskih istraživanja u Hrvatskoj u međunarodnoj znanstvenoj zajednici.

Povodom dvadesete obljetnice osnivanja *HKZ-a* održan je u *HAZU* 25. siječnja 2012. znanstveni skup *Kristalografija u Hrvatskoj*, s 32 priopćenja, te objavljen istoimeni zbornik radova u izdanju *HAZU* (2013.).

Članovi *HKZ-a* obilježili su *International Year of Crystallofraphy* (*IYCr2014*) nizom događanja: znanstveni skup *Suvremena kristalografija u Hrvatskoj* održan u *HAZU* 30. rujna 2014. (zbornik s 25 radova objavljen u *HAZU* 2015.), predavanja u *HAZU* i strukovnim udrugama, radovi u domaćoj i međunarodnoj periodici, *Hrvatsko-engleski rječnik kristalografije, fizike kondenzirane tvari i fizike materijala*. Pregled obilježavanja *IYCr2014* u Hrvatskoj nalazi se u prilogu ove knjige.

Potanki prikaz djelovanja hrvatskih kristalografa nalazi se u radu objavljenom u *Croatica Chemica Acta* **89** (2016) 367-370. Pojedinosti o djelatnostima, povijesti, članstvu i Odboru *HKZ*-a, te organizaciji prijašnjih znanstvenih skupova nalaze se na mrežnoj stranici http://www.hazu.hr/kristalografi.

Dvadeset peta obljetnica osnivanja *HKZ*-a obilježena je seminarom *Contemporary crystallography in Croatia,* koji je održan 20. travnja 2017. tijekom *25. hrvatskog skupa kemičara i kemijskih inženjera* (*25HSKIKI*), s međunarodnim sudjelovanjem, Poreč, 19.-22. travnja 2017. Program seminara bio je sljedeći:

– *Marijana Đaković*: Opening remarks (5 min)
– *Stanko Popović*: 25th anniversary of the foundation of Croatian Crystallographic Association (25 min)
– *Biserka Kojić – Prodić*: Frontiers in Crystallography (25 min)
– *Aleksandar Višnjevac*: Croatian Association of Crystallographers – five years of a tireless service to the Croatian crystallographers (15 min)
– *Jasminka Popović*: Thermosalient crystals (15 min)
– *Zoran Štefanić*: Macromolecular crystallography in my research (15 min)
– *Mario Cetina*: Closing remarks (5 min)

Sudionike seminara pozdravila je prof. dr. sc. Alessia Bacchi, predsjednica *Europske kristalografske zajednice*.

Osim pet priopćenja podnesenih na seminaru, članovi *HKZ*-a podnijeli su još 35 usmenih i posterskih priopćenja uvrštenih u program *25HSKIKI*. Sažetci tih priopćenja nalaze se u ovoj knjizi.

Razred za matematičke, fizičke i kemijske znanosti suglasio se s objavljivanjem knjige sažetaka priopćenja koja su podnijeli članovi *HKZ*-a tijekom *25HSKIKI*, pod naslovom

Dvadeset peta obljetnica osnutka Znanstvenoga vijeća za kristalografiju HAZU–Hrvatske kristalografske zajednice – Sažetci priopćenja na seminaru Suvremena kristalografija u Hrvatskoj, Poreč 2017.

Uprava *Hrvatske akademije znanosti i umjetnosti* odobrila je 22. svibnja 2017. tiskanje knjige sažetaka pod gornjim naslovom.

Urednici:

Prof. dr. sc. Dubravka Matković-Čalogović, članica suradnica *HAZU*, predsjednica *HKZ-a*

Prof. dr. sc. Marijana Đaković, tajnica *HKZ-a*

Prof. dr. sc. Stanko Popović, prof. em., redoviti član *HAZU*, član *HKZ-a*

Contents

Sadržaj

SEMINAR
CONTEMPORARY CRYSTALLOGRAPHY IN CROATIA
SUVREMENA KRISTALOGRAFIJA U HRVATSKOJ

25TH ANNIVERSARY OF THE FOUNDATION OF THE CROATIAN CRYSTALLOGRAPHIC ASSOCIATION

Dvadeset peta obljetnica osnutka Hrvatske kristalografske zajednice

Stanko Popović [1,2]

[1]*Croatian Academy of Sciences and Arts, Croatia*
[2]*Physics Department, Faculty of Science, University of Zagreb, Croatia*
E-mail: spopovic@phy.hr

Crystallography in Croatia began with courses in mineralogy in the last decades of the 19th century. *M. Paić* used powder diffraction in his PhD studies at Sorbonne in the 1930's. In 1948, *D. Grdenić* introduced X-ray crystal structure analysis in Zagreb. In 1966, the *Yugoslav Centre of Crystallography* (*YCCr*) was founded, acting under the auspices of the *Yugoslav Academy of Sciences and Arts*, Zagreb. *D. Grdenić* was elected president of *YCCr. YCCr* joined the *International Union of Crystallography* (*IUCr*) and the *European Crystallographic Association* (*ECA*). Until 1991, *YCCr* organized 25 annual and six *Italian-Yugoslav conferences* and the *13th European Crystallographic Meeting* (*ECM13*). In that period, 25 issues of the journal *Annual of the YCCr* were published.

After the proclamation of independence of Croatia, the *Croatian Academy of Sciences and* Arts (*CASA*) founded, on February 28*th*, 1992, *the Scientific Council for Crystallography of CASA–Croatian Crystallographic Association* (*CCA*; *Hrvatska kristalografaka zajednica*, *HKZ*). *B. Kamenar* was elected president, who was followed by *S. Popović* in 2006 and *D. Matković Čalogović* in 2016. *CCA* soon joined *ECA* and *IUCr*. Since 1992, *CCA* and the *Slovenian Crystallographic Society* have been organizing annual *Croatian-Slovenian/Slovenian-Croatian Crystallographic Meetings,* with international participation, alternately in Croatia and in Slovenia. Twenty five meetings have been held so far. The reports on the meetings have been published in the *IUCr Newsletter.* Members of *CCA* edited a special issue of *Croatica Chemica Acta*, **82** (2009), dedicated to *D. Grdenić* on occasion of his 90th birthday. An extended essay on activities and achievements of *CCA* was published in *IUCr Newsletter*, **19** (2011). Today, about one hundred twenty scientists are members of *CCA* studying structure of biologically active substances, proteins, organometallic compounds, pharmaceuticals, microstructure of composites, in relation to physical, chemical and biological properties.

In August 2011, the *ECA Council* decided that the *ECM29* would be held in Rovinj in 2015. That was a great recognition of achievements in Croatia by the international scientific community. In September 2012, the organization of *ECM29* was undertaken by the *Croatian Association of Crystallographers* (*CAC*, emerged from the previous *Organizing Committee* elected by *CCA*), as approved by the *Assembly* of *CCA*. *ECM29* was a great success, being the largest scientific meeting in natural sciences ever held in Croatia.

During the *International Year of Crystallography*, Croatian crystallographers performed a series activities, among others: 1) scientific meeting *Contemporary Crystallography in Croatia*, the corresponding Proceedings published by *CASA*; 2) *English-Croatian Dictionary of Crystallography, Physics of Condensed Matter and Materials Science,* containing 1710 terms with short description of each term; 3) *Crystal-growing competition* organized by *CAC, CCA* and *PLIVA*, participants being pupils in secondary schools; 4) review papers in *Kemija u industriji, Priroda*, *Angewandte Chemie Int. Ed.*

More details in: *Croat. Chem. Acta* **89** (2016) 367-370; http://www.hazu.hr/kristalografi/

FRONTIERS IN CRYSTALLOGRAPHY

Suvremene teme kristalografije

Biserka Kojić-Prodić

Ruđer Bošković Institute, Zagreb, Croatia
E-mail: kojic@irb.hr

X-ray crystallography provides an essential way of determining the structure of matter at the atomic resolution. The molecular structure reveals 3D-arrangements of atoms defined by interatomic interactions – chemical bonds. Intra- and intermolecular forces define the chemical and physical properties of molecules ranging from small inorganic and organic molecules to proteins and their large complexes building the macromolecular machineries of life. In chemical reactions and life processes extremely fast reaction mechanisms are involved, even at femto and atto-timescale. It has been a challenge to follow such reactions in *statu nascendi*. The use of X-ray free electron lasers enables recording of ultrafast processes and to study their dynamics. Particularly important is an insight into dynamics of electron structures of molecules. In the area of non-ambient X-ray crystallography many technological advancements are exploited to recognise the influence of high pressure, temperature and atmosphere on molecular interactions within a crystal. For the interpretation of time-resolved images a very powerful algorithms and computers have been developed. An advancement of sensitive and ultra-fast detectors has been a great challenge for manufacturers. Their importance in all areas of X-ray diffraction is more than evident, however, the most demanding requirements are in laser-crystallography - XFELs, nonambient crystallography, and charge-density studies. Among these three areas, being the hot topics of current crystallography, charge density studies have started a few decades earlier than the others two. Nowadays, the power of the method is enormous: more sophisticated experiments and algorithms assisted by theoretical chemistry methods enable the detailed interpretation of the electron distribution, that can lead to a revision of the old concepts and to introduce the new ones of the nature of chemical bond and non-bonding interactions. Crystallography as an interdisciplinary science contributes to progress of chemistry, materials science, biology, medicine, pharmacology, agronomy, geosciences, ecology, and technology. Enormous progress of computer technology, X-ray sources (new generations of synchrotrons, X-ray free electron lasers-XFELs) and sensitive and fast detectors support new, powerful experimental methods, which all together, provide detailed images of molecular systems and their dynamics. These cutting-edge researches have opened up new directions in science and technology.

CROATIAN ASSOCIATION OF CRYSTALLOGRAPHERS – FIVE YEARS OF A TIRELESS SERVICE TO THE CROATIAN CRYSTALLOGRAPHERS

Hrvatska udruga kristalografa-pet godina neumorno u službi hrvatskih kristalografa

Aleksandar Višnjevac

Ruđer Bošković Institute, Zagreb, Croatia

Croatian Association of Crystallographers (CAC) is a professional association founded on Aug. 24th, 2012 with an objective to endorse excellence, encourage co-operation, facilitate international contacts and exchange and support career developments within the Croatian crystallographic community, as well as to promote the achievements and importance of crystallography towards the general public. These goals are being achieved by an intense programme of international workshops, summer schools, seminars, conferences and other scientific and professional gatherings, as well as educational activities oriented towards the school children and promotional activities in the mainstream media. The ultimate goal of all our activities is to position Croatia as a regional stronghold of the research and education in crystallography and related disciplines.

In order to tackle fascinating recent achievements and developments, which, over the last two decades, put crystallography to the front lines of the natural sciences, CAC has developed a unique workshop concept under the brand **Hot Topics in Contemporary Crystallography (HTCC)**. The workshop is intended to the utterly ambitious PhD students and postdocs, as well as to the young crystallographers in the early stages of their autonomous careers, conducting their research within a broad spectrum of disciplines and sub disciplines related to crystallography. The first edition – HTCC2014, with six lecturers and 27 students, was held from May 10*th* to 15*th*, 2014 in Šibenik, Croatia, and it was a central event to mark the UN proclaimed International year of crystallography (IYCr2017) in Croatia. The second edition - HTCC2017, is to be held in Poreč, from Apr. 22*nd* to 26*th*, 2017 with the participation of eight lecturers and 25 students. The three hot topics to be discussed are: (*i*) dynamic crystallography, (*ii*) crystallography under non-ambient conditions, and (*iii*) charge density studies.

In 2014 and in 2017, CAC has, with the generous support of Pliva Inc. – member of TEVA group, together with Croatian Crystallographic Association, co-organized the school contest in crystal growth called "**The beauty of crystal faces**" intended to elementary and secondary school students across Croatia. Both contests were amazingly popular, as more than 150 schools from all parts of Croatia took part in both contests. First, the propositions and categories of the contest are defined and published. The chemicals needed for the crystal growth experiments are then distributed by courier to those who had applied, the school teams led by chemistry/physics teachers are founded, and the crystal growth experiments are being conducted onsite. The schools ship the produced crystals to the project headquarters, where our experienced crystallographers assisted by motivated chemistry students examine the submitted materials and choose the best in all categories. Finally, the most successful teams are invited to Zagreb and awarded at the special closing ceremony.

Two big international crystallographic meetings were recently held in Croatia, organized immaculately by the Croatian Association of Crystallographers. **3*rd* European Crystallographic**

School (ECS3), organized jointly by European Crystallographic Association (ECA) and CAC, was held in Bol, Croatia, from Sep. 25th to Nov. 2nd, 2016 with 116 registered participants. **29th European Crystallographic Meeting (ECM29)**, organized jointly by CAC and ECA was held under the patronage of the Ministry of science, education and sports of the Republic of Croatia, in Rovinj, Croatia, from Aug. 23rd to Aug. 28th, 2015. For the first time in history of ECMs, the opening ceremony, as well as the Perutz prize lecture, were live web streamed. *1050 crystallographers from 51 countries* and from all *six continents* participated at the ECM29. ECM had 785 scientific contributions distributed among 51 microsymposia, 14 KN lectures and two plenary lectures. It also featured 10 satellite meetings and 20 poster prizes. By many of these numbers, ECM29 beat the historic records.

We, in Croatian Association of Crystallographers, deeply understand the necessity of science communication and outreach, as a way to create a favourable and positive attitude amongst general public and, consequently, among the policy makers, towards fundamental science, research and technology. We also understand the necessity of the active promotion of the achievements and potential of crystallography within the context of the traditional disciplines such as chemistry, physics and molecular biology. Therefore, we continuously appear in the mainstream media (particularly in the programmes of the Croatian public radio and television) promoting crystallography, explaining its achievements and importance for the technological development, and presenting hereby quoted and other ongoing and future projects. At the 25HSKIKI – the 25th Croatian meeting of chemists and chemical engineers, CAC has a poster award for the best poster among those presenting research supported by crystallographic methods and techniques.

Future projects are not less ambitious. From Sep. 2017 to Sep. 2018 CAC shall, endorsed by the city of Zagreb, organize a series of ten monthly seminars under the brand name **International crystallographic seminars in Zagreb**, where the successful PhD students and postdocs working in the field of crystallography and related disciplines at the universities and public research centres across the region of South Eastern Europe will have the opportunity to present their research. Croatian Association of Crystallographers is also preparing the bid for the organization of the EPDIC17 (European powder diffraction conference) to be held in Šibenik in 2020, in the brand new "Šibenik Convention Centre", the biggest conference centre in Croatia. The support of the City of Šibenik and the local tourist board is already secured. Over 500 crystallographers from all over Europe are expected at this conference.

THERMOSALIENT EFFECT – CRYSTALS THAT EXHIBIT ACROBATIC BEHAVIOUR

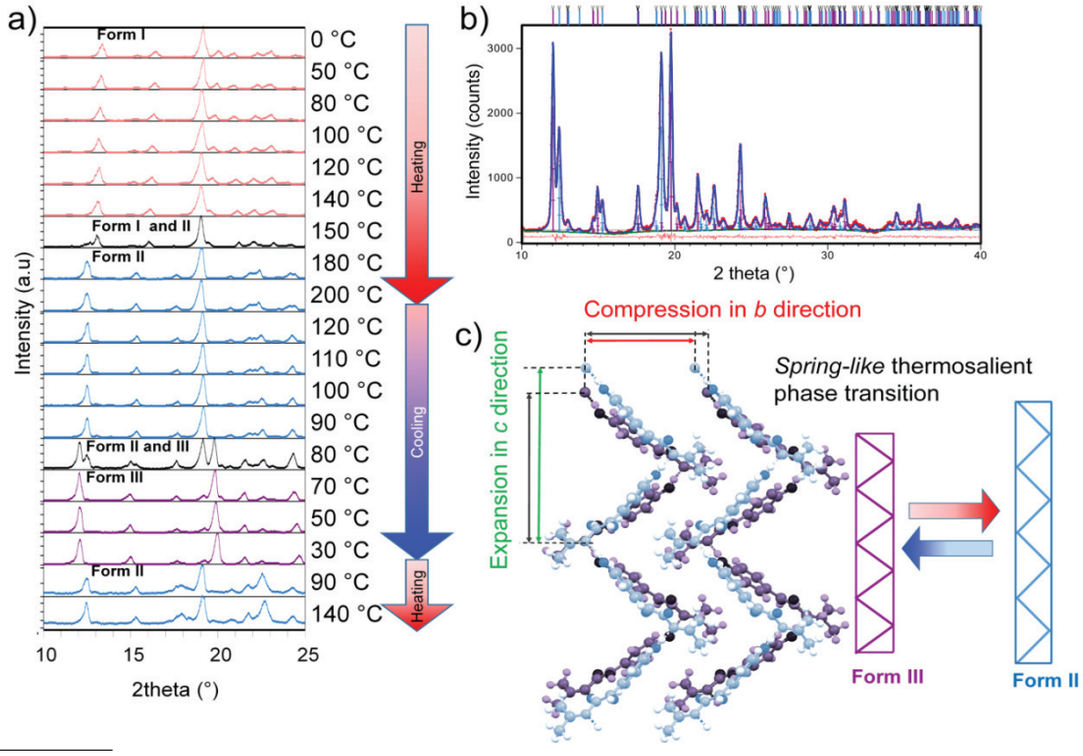
Termoodskočni efekt – kristali s akrobatskim ponašanjem

Željko Skoko[a], Jasminka Popović[b], Ivor Lončarić[a]

[a]*Department of Physics, Faculty of Science, University of Zagreb, Bijenička c. 32, 10000 Zagreb, Croatia*

[b]*Ruđer Bošković Institute, Bijenička c. 54, 10000 Zagreb, Croatia*

Organic crystals exhibit many appealing features, but one does not expect them to perform acrobatics, which can be expressed in the form of jumping, twisting, rolling, curling, etc. But this is actually what happens with the special species of crystals named thermosalient crystals. Thermosalient crystals are materials that undergo topotactic phase transition during heating/cooling which is so agile and energetic that crystals literally jump off the stage to heights that are several times larger than their own dimensions. Apart from being visually extremely attractive and thus providing an excellent example of the natural transformation of thermal energy into mechanical work, these materials also present huge technological potential for targeted production of nanoswitches, nanoactuators, thermal sensors or artificial muscles[1]. This effect is quite rare and is usually serendipitously observed, hence there have been only a dozen reported thermosalient systems. The explanation of this phenomenon is quite cumbersome, because it is difficult to retain the crystal's integrity after the thermosalient phase transition. So far, all the studies of the thermosalient phenomenon were based on the experimental techniques, but it seems that this is not enough for the full elucidation of the phenomenon, and theoretical investigations should be coupled with the experimental results.



[1] *J. Am. Chem. Soc.*, **2010**, *132* (40), pp 14191–14202

Figure 1 a) Thermally induced phase transitions of *N*'-2-propylidene-4-hydroxybenzohydrazide. XRPD patterns of Form I are shown in peach, Form II in light blue, while the XRPD patterns of Form III in purple**. b)** Rietveld refinement of powder data collected at 77 °C (during the cooling cycle). Experimental data are shown as red line, calculated diffraction pattern as blue line, while the difference curve is given below (in red). Purple vertical lines represent positions of Bragg reflections for Form III while diffraction line positions of Form II are given as light blue vertical marks. **c)** Spring-like thermosalient phase transition between Form III and Form II in *bc* plane. Only parallel, symmetry equivalent, zig-zag chains are shown.

Here we present a combined experimental and theoretical study of the thermosalient effect in the *N*-2-propylidene-4-hydroxybenzohydrazide, which shows not one but three thermosalient phase transitions previously unreported in the literature. This is, to the best of our knowledge, the first attempt to theoretically decipher the jumping crystals effect. As in most of the thermosalient systems, immense negative thermal expansion seems to be the most likely candidate for the driving force behind the phenomenon. Our results show that it is the direct consequence of the elastic properties of the crystal which exhibits uniaxial negative compressibility. Furthermore, these properties are also determining the reversibilities/irreversibilities of the phase transitions in this system. And in conclusion, we propose a new mechanism of the thermosalient effect in this system, based on the excitations of the low-energy phonons which provide energy needed for the crystal to overcome the energy barrier between the phases.

MACROMOLECULAR CRYSTALLOGRAPHY IN MY RESEARCH

Makromolekulska kristalografija u mojem istraživanju

Zoran Štefanić

Ruđer Bošković Institute, Zagreb, Croatia
E-mail: zoran.stefanic@irb.hr

Macromolecular X-ray crystallography has always been, and still remains the most important method for obtaining high resolution data on all macromolecular structures, such as proteins and nucleic acids and their complexes. This is confirmed by the number of structures obtained by X-ray crystallography deposited in the Protein Data Bank[1] with respect to two other significant methods, although the other methods are steadily gaining in importance (115335 X-ray structures compared to 11796 solved by NMR and 1457 solved by electron microscopy). In this brief talk I will outline some of the uses of macromolecular crystallography as part of our own research.[2]

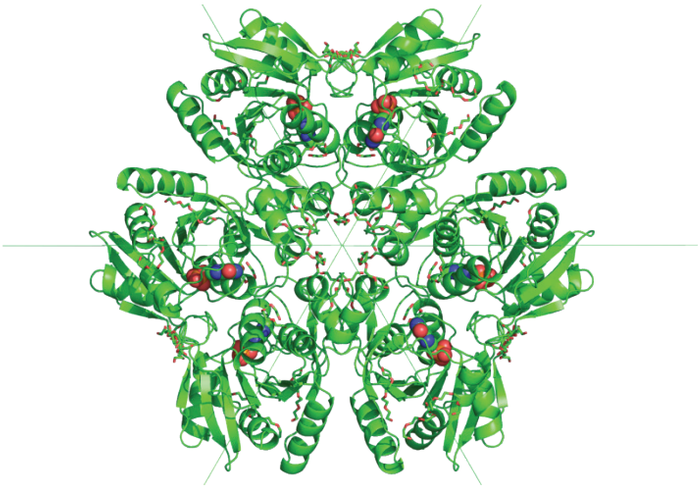


Figure 1: Hexameric structure of purine nucleoside phosphorylase (PNP) from human pathogen *H. Pylori*, determined in our laboratory recently, is one of a few to exhibit perfect 32 point group symmetry.

References

[1] H.M. Berman, J. Westbrook, Z. Feng, G. Gilliland, T. N. Bhat, H. Weissig, I. N. Shindyalov, P. E. Bourne. *The Protein Data Bank Nucleic Acids Research*, **28** (2000) 235-242.

[2] Z. Štefanić, G. Mikleušević, M. Luić, A. Bzowska, I. L. Ašler, *Int J Biol Macromol*. 2017: S0141-8130(17)30233-7. doi: 10.1016/j.ijbiomac.2017.03.101.

ORAL CONTRIBUTIONS
USMENA IZLAGANJA

QUANTITATIVE *IN SITU* MONITORING AS A TOOL TO STUDY MECHANISMS OF MECHANOCHEMICAL MILLING REACTIONS

Kvantitativne tehnike *in situ* u otkrivanju mehanizama mehanokemijskih reakcija mljevenjem

Ivan Halasz, Stipe Lukin, Krunoslav Užarević

Ruđer Bošković Institute, Zagreb, Croatia
E-mail: ivan.halasz@irb.hr

We will here describe the development of mechanistic understanding from the first *in situ* monitoring by synchrotron powder X-ray diffraction [1,2], followed by laboratory Raman *in situ* monitoring [3,4] and finally focus on the most recent quantitative evaluation from tandem *in situ* monitoring combining the two techniques in a high-throughput approach enabling quantitative assessment and kinetic analysis even in systems involving novel and short-lived phases of unknown crystal structures. These recent results provide the necessary infrastructure for a thorough mechanistic description of mechanochemical milling reactions which was thus far hindered mainly by the inability of their quantitative evaluation. We will address also the issue of the temperature of the reaction mixture and its influence of reaction kinetics and mechanisms. Tandem in situ monitoring via PXRD and Raman spectroscopy, applied to cocrystallisation of nicotinamide and benzoic acid, revealed a rich polymorphic system with multiple phase transitions and a variety of reaction pathways that can be altered and controlled by the type of the liquid additive as well as by its amount. For the first time, we observe a decelerating effect of the liquid additive on LAG reaction kinetics. Quantitative assessment from tandem in situ monitoring, performed in seconds-time resolution, establishes by extension quantitative *in situ* Raman monitoring as a quantitative technique that is readily implemented in a conventional laboratory.

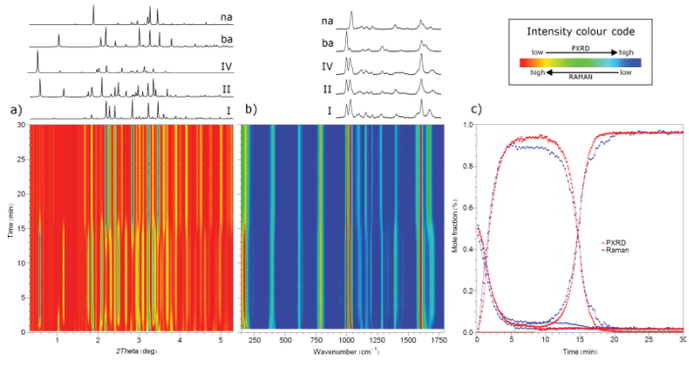


Figure 1: (a) PXRD and (b) Raman *in situ* monitoring and (c) their comparison

References

[1] T. Friščić, I. Halasz, P.J. Beldon, A.M. Belenguer, F. Adams, S.A.J. Kimber, V. Honkimäki and R.E. Dinnebier, *Nature Chem.* **5** (2013) 66-73.

[2] I. Halasz, T. Friščić, S.A.J. Kimber, K. Užarević, A. Puškarić, C. Mottillo, P. Julien, V. Štrukil, V. Honkimäki and R.E. Dinnebier, *Faraday Discuss.* **170** (2014) 203-221.

[3] D. Gracin, V. Štrukil, T. Friščić, I. Halasz and K. Užarević, *Angew. Chem. Int. Ed.* **53** (2014) 6193-6197.

[4] M. Tireli, M. Juribašić Kulcsar, N. Cindro, D. Gracin, N. Biliškov, M. Borovina, M. Ćurić, I. Halasz and K. Užarević, *Chem. Commun.* **51** (2015) 8058-8061.

SEMIQUINONE RADICALS AS A BASE FOR NOVEL ORGANIC (SEMI) CONDUCTORS: HOW π-STACKING DETERMINES MAGNETISM AND ELECTRICAL CONDUCTIVITY

Semikinonski radikali kao temelj za nove organske (polu)vodiče: utjecaj π-interakcijâ na magnetska svojstva i električnu vodljivost

Krešimir Molčanov,[1] Ana Šantić,[1] Vladimir Stilinović[2], Biserka Kojić-Prodić[1]

[1]*Ruđer Bošković Institute, Zagreb, Croatia*

[2]*Department of Chemistry, Faculty of Science, University of Zagrebu, Croatia*
E-mail: kmolcano@irb.hr

Semiquinones are a class of stable organic radicals with a great potential for design of novel organic electronics and multifunctional materials. Since the radicals are planar, they typically form π-stacks, which stabilise crystal packing and determine magnetic and electrical properties of the crystals. Stronger π interactions thus imply stronger exchange interactions and lower energy barrier for electron transfer. Two types of π-stacks have been described: 1) Peierls-distorted with alternating short (< 3.1 Å) and long (> 3.35 Å) [1] interplanar distances (i.e. comprising dimers of radicals with paired spins), which are diamagnetic and isolators, and 2) stacks of equidistant radicals which are 1D antiferromagnetic and semiconductors [2].

Despite its importance, π-stacking of planar organic radicals has been little studied from the fundamental point of view. Here we present a detailed study of different factors which influence (semi)conductivity of semiquinone systems in the solid state: 1) type of stack (Peierls-distorted or equidistant), 2) induction effect of electron-withdrawing substituents, 3) interplanar distance, and 4) orientation of the stacked rings. As suitable systems we chose series of salts of three semiquinones (5,6-dichloro-2,3-dicyanosemiquinone [3], tetrachloro- and tetrabromosemiquinone [1]) with planar organic cations derived from *N*-methylpyridinium [2].

Since only antiferromagnetic compounds with equidistant radicals are good semiconductors, we focused our attention to this type of stacks. Electronegativity (i.e. electron-withdrawing) of the substituents plays a double role: *i*) it stabilises the radical by enhancing delocalisation of π electrons and *ii*) lowers the energy of the HOMO orbital, thus increasing band gap related to electronic transport. Therefore, the most stable radicals (5,6-dichloro-2,3-dicyanosemiquinone, DDQ [3]) are the least conductive, while less stable ones (tetrabromosemiquinone) are the best conductors. This effect is far more pronounced than increasing of the band gap by increasing interplanar separation, while orientation of the rings in the stacks apparently does not influence electrical conductivity.

Reference

[1] K. Molčanov, B. Kojić-Prodić, D. Babić, D. Pajić, N. Novosel and K. Zadro, *CrystEngComm* **14** (2012) 7958–7964.

[2] K. Molčanov, V. Stilinović, A. Šantić, N. Maltar-Strmečki, D. Pajić and B. Kojić-Prodić, *Cryst. Growth Des.* **16** (2016) 4777–4782.

[3] K. Molčanov, D. Babić, B. Kojić-Prodić, J. Stare, N. Maltar-Strmečki and L. Androš Dubraja, *Acta Crystallogr.* **B70** (2014) 181–190.

SUPRAMOLECULAR POTENTIAL OF HALOGEN INTERACTIONS IN METAL-ORGANIC SYSTEMS OF Co^{II} AND Ni^{II} PENTANE-2,4-DIONATO COMPLEXES

Supramolekulski potencijal halogenskih interakcija u metalo-organskim sustavima kompleksa Co^{II} i Ni^{II} s pentan-2,4-dionom

Mladen Borovina,[1] Ivan Kodrin[1], Marijana Đaković[1]

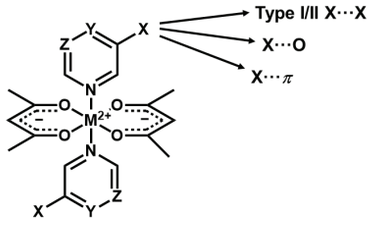
[1]*Department of Chemistry, Faculty of Science, University of Zagreb; Horvatovac 102a, Zagreb, Croatia*

E-mail: mborovina@chem.pmf.hr

In recent years the crystal engineering potential of halogen bonds was recognized and extensive research is being carried out to maximally utilize those interactions in engineering organic and metal-organic systems. It was even shown that in some cases it is possible to predict the halogen patterns according to electrostatic potential values calculated for each potential donor and acceptor [1]. Halogen atoms can also form other, weaker supramolecular interactions such as halogen···π and C–H···halogen interactions. Although their usual role in the crystal packing is only secondary, it was shown that they can become main structure directing interactions in systems lacking strong hydrogen and halogen bonding capability [2].

We have recently reported our findings of type-I halogen···halogen and halogen···π interactions present in a series of six isostructural pentan-2,4-dionato Co(II) and Ni(II) complexes with chloro-, bromo- and iodopyrazine. It was found that halogen···π interactions play a secondary role in the packing while type-I interactions arise as the result of the packing itself [3]. In order to assess possible steric effects as well as to determine the impact of electron withdrawing power of endocyclic nitrogen atoms on the overall halogen bond pattern formation, here we opted to examine a series of halopyrimidine derivates.

To this aim we have prepared Co(II) and Ni(II) pentane-2,4-ditionato complexes with iodopyridine and bromopyrimidine. The crystal packing of iodopyridine derivates is directed by I···O halogen bonds, while in the crystal structure of bromopyrimidine derivatives halogen···π interactions were observed.



Ligand	Halogen interaction status
	I···O
 X=Cl, Br, I	X···π & Type I
	X···π

Acknowledgments

This work has been fully supported by Croatian Science Foundation under the project UIP-11-2013-1809.

References

[1] C.B. Aakeroy, T.K. Wijethunga, J. Desper and M. Đaković, *Cryst. Growth Des.* **15** (2015) 3853−3861.

[2] R. Bishop, M.L. Scudder, C.D. Craig, A. Noman, M.M. Rahman and S.F. Alshahateet, *Mol. Cryst. Liq. Cryst.* **440** (2005) 173–186.

[3] M. Borovina, I. Kodrin and M. Đaković; *24th Cro-Slo Cryst Meeting, Bol 2016, Book of Abstracts*, Croatian Crystallographic Association, Croatian Academy of Sciences and Arts, Zagreb, 11–11.

INVESTIGATION OF MIXED GLASS FORMER EFFECT AND THERMALLY INDUCED CRYSTALLIZATION IN Li_2O-P_2O_5-GeO_2 GLASSES

Istraživanje efekta miješanih staklotvoraca i termički potaknute kristalizacije stakala Li_2O-P_2O_5-GeO_2

Kristina Sklepić,[1] Petr Mošner,[2] Gregory Tricot,[3] Željko Skoko,[4] Ladislav Koudelka,[2] Andrea Moguš-Milanković[1]

[1]*Ruđer Bošković Institute, Division of Materials Chemistry, 10000 Zagreb, Croatia*
[2]*Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, 53210 Pardubice, Czech Republic*
[3]*Unité de Catalyse et Chimie du Solide, Universite de Lille1, 59655 Villeneuve d'Ascq, France*

[4]*Department of Physics, Faculty of Science, University of Zagreb, 10000, Zagreb, Croatia*
E-mail: ksklepic@irb.hr

In order to improve the stability, safety and required performance of lithium-ion batteries many novel glass and glass-ceramic materials are being investigated for their potential use as a solid electrolytes [1,2].

Ternary ion conducting $40Li_2O–(60\text{-}x)P_2O_5–xGeO_2$, x=0–25 mol%, glasses have been chosen as a model glass system for the mixed glass former effect and crystallization investigations. Electrical properties of these glasses were studied by impedance spectroscopy (IS) to determine the influence of the structural changes induced by gradual substitution of one glass network former, P_2O_5, by other network former, GeO_2, keeping Li^+ ion content constant. Glass-ceramics have been prepared by controlled crystallization of these glasses at different temperatures selected according to the DTA curves. Changes that occurred in structure and electrical properties of glass-ceramics were analysed.

In glasses, the dc conductivity increases for the three orders of magnitude with increasing germanium content. This conductivity enhancement was attributed to the facilitated mobility of Li^+ ions due to the depolymerisation of phosphate chains and incorporation of germanium atoms into network, confirmed by Raman and MAS NMR. Heat-treated glasses have been characterized using XRD and MAS NMR. Microstructure study showed crystalline grains embedded into glass matrix. Grain size and degree of crystallinity varies with germanium content and crystallization temperatures. Heat-treated GeO_2-free samples showed slightly higher dc conductivity values than the non-treated glasses. On the other hand, when germanium oxide was added into the system, the dc conductivities of heat-treated samples showed lower values if compared with values obtained for glasses. The decrease in dc conductivity is more pronounced for samples with high germanium content and higher degree of crystallinity. Correlated behaviour between conductivity and changes in microstructure indicates that in the heat-treated glasses a part of the Li^+ ions enters randomly distributed crystalline grains, which are not enough connected to form easy conducting pathways.

References

[1] C. Cao, Z.B. Li, X.L. Wang, X.B. Zhao and W.Q. Han, *Frontiers in Energy Research*, **2** (2014) 25(1-10).

[2] A. Moguš-Milanković, K. Sklepić, P. Mošner, L. Koudelka and P. Kalenda, *J. Phys. Chem. B*, **120(16)** (2016) 3978-3987.

FROM DISCRETE OR POLYMERIC HETEROMETALLIC COMPLEXES TO THE MIXED-METAL OXIDES

Od diskretnih ili polimernih heterometalnih kompleksa do mješovitih metalnih oksida

Marijana Jurić, Lidija Androš Dubraja, Jasminka Popović, Krešimir Molčanov

Ruđer Bošković Institute, Bijenička cesta 54, Zagreb, Croatia
E-mail: Marijana.Juric@irb.hr

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

The possibility of using coordination polymers through the thermal decomposition process as molecular precursors in the synthesis of nanomaterials with high surface and specific morphology has been considered only recently. This method of obtaining oxide materials, compared with conventional methods, has several advantages: (*i*) the obtained material is more homogeneous because the metals are mixed at the molecular level; (*ii*) the resulting materials have relatively high specific surface areas because the crystalline oxides are formed under significantly milder conditions than those in, for instance, solid-state reaction processes; (*iii*) the existence of bridging or chelating ligands in the precursors prevents metal separation during oxide formation; (*iv*) there is much greater control of the metal stoichiometry in the final oxide. The $C_2O_4^{2-}$ group easily decomposes to gaseous CO_2 and CO at low temperatures, and hence, the oxalate-based solids can serve as a convenient source of oxides [1].

Utilizing the preparation of the oxide materials *via* thermal decomposition, several oxalate-based compounds were tested as molecular precursors. Discrete heterotetranuclear oxo-bridged compound $[Cr_2(bpy)_4(\mu\text{-}O)_4Nb_2(C_2O_4)_4]\cdot 3H_2O$ (**1**; bpy = 2,2'-bipyridine) showed to be a good candidate for molecular precursor-to-material conversion, yielding the rutile-type $CrNbO_4$ oxide after heat treatment at 900°C. The thermal processing of heterodimetallic one-dimensional (1D) compound $\{[CaCr_2(bpy)_2(C_2O_4)_4]\cdot 0.83H_2O\}_n$ (**2**) proved to be a simple, one-step synthesis route for the preparation of the β-$CaCr_2O_4$ phase at 1100 °C in nitrogen flow. The r.t. structure of β-$CaCr_2O_4$ is isomorphic with calcium ferrite, unlike most chromate structures, which usually crystallize as spinel oxides. A three-dimensional (3D) oxalate-based coordination polymer $\{[Co(bpy)_3][Mn_2(C_2O_4)_3]\cdot H_2O\}_n$ (**3**) was used as a single-source precursor for the formation of spinel oxide $CoMn_2O_4$ heating at 800 °C.

The conversion *via* thermal decomposition of compounds **1**–**3** was explored by thermal analysis (TGA and DTA), IR spectroscopy and powder X-ray diffraction (PXRD).

References

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

ONE-POT THREE-COMPONENT MECHANOSYNTHESIS OF IMINE COCRYSTALS WITH HALOGEN BOND DONORS

Kokristali imina s donorima halogenske veze dobiveni trokomponentnom mehanokemijskom sintezom u jednom koraku

Marija Zbačnik, Matea Vitković, Dominik Cinčić

Department of Chemistry, Faculty of Science, University of Zagreb, Zagreb, Croatia
E-mail: mzbacnik@chem.pmf.hr

A century long interest in *o*-hydroxy imines can be attributed to their photo- and/or thermochromic properties in the solid state [1] which can be tuned by means of cocrystallization [2,3].

Herein we report one-pot mechanosynthesis which combines the formation of covalent bonds and halogen bonds [4] to obtain imine cocrystals with halogen bond donors. In order to explore the potential of pyridyl fragments as halogen bond acceptor species in comparison/competition with hydroxy and methoxy groups [3] we used imines derived from *o*-vanillin (**ov**) and aminopyridines (**3amp** and **4amp**) and as halogen bond donors we selected commonly used perfluorinated compounds: 1,2-, 1,3- and 1,4-diiodotetrafluorobenzene (**12tfib**, **13tfib** and **14tfib**) as well as 1,3,5-triiodotrifluorobenzene (**135titfb**). We obtained eight cocrystals by one-pot grinding of a mixture of **ov**, aminopyridine and halogen bond donors in 1:1:1 or 2:2:1 molar ratios. To observe mechanosynthesis, as well as to facilitate the characterization of the new cocrystal by single-crystal X-ray diffraction, mechanochemical experiments were accompanied by crystallization. All reactants and products were characterized by means of powder X-ray diffraction. In all obtained cocrystals the molecules are connected by means of I···N halogen bonds between halogen bond donor iodine atoms and pyridine nitrogen atoms.

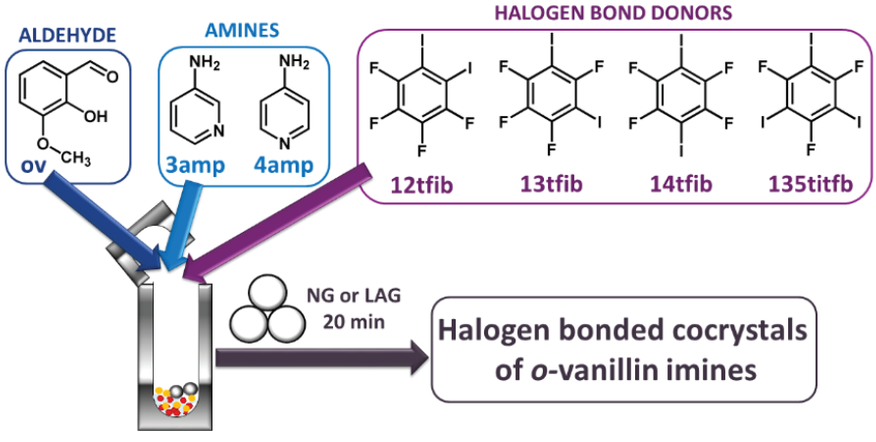


Figure 1: A schematic view of the methodology used for one-pot mechanosynthesis of the cocrystals.

References

[1] E. Hadjoudis and I.M. Mavridis, *Chem. Soc. Rev.* **33** (2004) 579-588.

[2] A. Carletta, X. Buol, T. Leyssens, B. Champagne and J. Wouters, *J. Phys. Chem. C* **120** (2016) 10001-10008.

[3] M. Zbačnik, M. Vitković, V. Vulić, I. Nogalo and D. Cinčić, *Cryst. Growth Des.* **16** (2016) 6381-6389.

[4] D. Cinčić and T. Friščić, *CrystEngComm* **16** (2014) 10169-10172.

BEAUTY OF CRYSTAL FACES: THE STORY OF GROWING SINGLE CRYSTALS

Ljepota kristalnih ploha: Kako uzgojiti jedinični kristal

Alen Bjelopetrović,[1] Ernest Meštrović,[2] Lucija Papa,[3] Tomislav Lež,[3] Toni Lijić,[3] Hana Alborghetti,[2] Aleksandar Višnjevac,[1] Krešimir Molčanov[1]

[1]*Ruđer Bošković Institute, Bijenička cesta 54, 10 000 Zagreb, Croatia*
[2]*PLIVA, Research and Development, Prilaz Baruna Filipovića 29, 10 000 Zagreb, Croatia*
[3]*University of Zagreb, Faculty of Science, Chemistry Department, Horvatovac 102a, 10 000 Zagreb, Croatia*

E-mail: abjelop@irb.hr

Croatian Association of Crystallographs and Croatian Crystallographic Association in cooperation with PLIVA and Chemistry Department, Faculty of Science, University of Zagreb have devised and organized 2nd Croatian contest in growing single crystals for students of elementary and secondary schools entitled "The Beauty of Crystal faces". This contest was intended for students of 7th and 8th grade of the elementary school and for all four grades of the secondary school. The main goal of the contest was preparation of a single crystal as big as possible in one of three categories: 1) inorganic salt crystallization, 2) organic salt crystallization and 3) challenging category in which students first had to prepare the substance from which they would grow their single crystal. The students of primary and secondary schools were competed separately and duration of the experiment was limited to two months. One of primary goals of the contest has been to bring the world of science closer to students and to arose their interest about crystals, crystal growth as well as to teach them scientific approach to a real problem. Through the contest the students had to adopt fundamental techniques and procedures used in a chemical laboratory such as using laboratory dishes and chemicals, filtration, decanting, handling acids and bases and writing high-quality laboratory notebook, which is an important component of the experimental work.

The response to the content was unexpectedly good: there were more than 100 schools applied with more than 700 students divided in about 170 teams. This contest indicated that a lot of students already have great interest toward chemistry, science in general and experimental work.

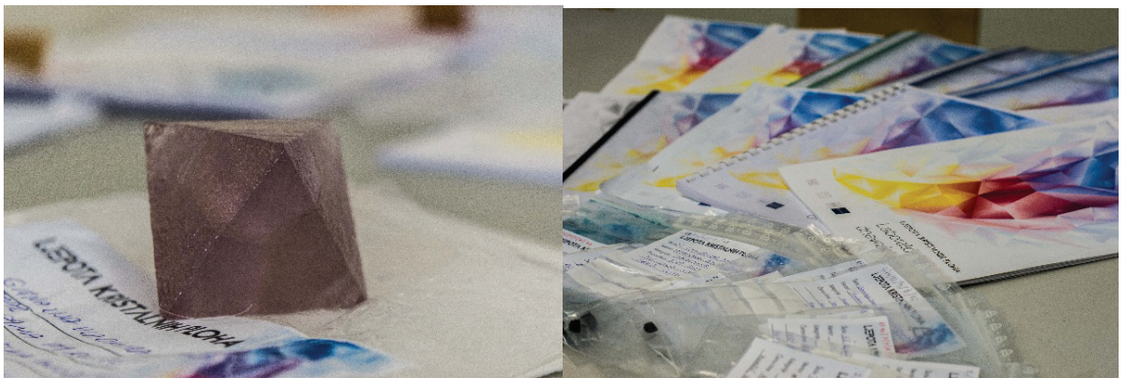


Figure 1: Assessment and grading of submitted crystals prepared by students.

POSTER PRESENTATIONS
POSTERSKE PREZENTACIJE

COMPUTATIONALLY GUIDED SEARCH FOR NOVEL BENZIMIDAZOLE DERIVATIVES WITH ENHANCED ANTIPROLIFERATIVE ACTIVITY

Dizajn benzimidazolnih derivata izražene antiproliferativne aktivnosti temeljen na rezultatima računalnih metoda

Branimir Bertoša,[1] Darko Vušak,[1] Nataša Perin,[2] Irena Martin-Kleiner,[3] Marijeta Kralj,[3] Grace Karminski-Zamola,[2] Marijana Hranjec[2]

[1]*Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10 000 Zagreb, Croatia*

[2]*Department of Organic Chemistry, Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 20, 10 000 Zagreb, Croatia*

[3]*Division of Molecular Medicine, Ruđer Bošković Institute, Bijenička cesta 54, 10 000 Zagreb, Croatia*

E-mail: bbertosa@chem.pmf.hr

The experimental search for novel benzimidazole derivatives with enhanced antiproliferative activity was successfully guided by QSAR modelling. Robust 3D-QSAR models were derived using available database of the compounds with previously measured activities in the same laboratory, under the same conditions. Using the QSAR analysis of the obtained models, the molecular descriptors with the highest influence on the activity were identified. The QSAR analysis revealed that the antiproliferative activities against four cell lines, H460, HCT 116, MCF-7, and SW 620, should be increased if the new compounds are charged at pH range from 5 to 7 and if their hydrophobicity is increased comparing to the dataset compounds. Novel amino and diamino substituted benzimidazo[1,2-*a*]quinolines with introduced quarter amino groups and aliphatic chains were designed according to the QSAR analysis and their antiproliferative activities were computationally predicted. Using uncatalyzed microwave assisted amination, 14 novel compounds were synthesized and their antiproliferative activities were assessed against H460, HCT 116, MCF-7, and SW 620 tumor cell lines *in vitro*. Novel compounds showed antiproliferative activities in micromolar and submicromolar inhibition concentrations. Experimental measurements of antiproliferative activities enabled undisputed validation of QSAR models, very good agreement between experimentally measured activities and computational predictions was obtained. Based on the identified molecular descriptors with the highest influence on antiproliferative activity, possible mode of action is proposed.

APPLICATION OF NEW CHIRAL PHOSPINE Rh(I) COMPLEXES IN ENANTIOSELECTIVE CATALYTIC HYDROGENATION REACTIONS

Primjena novih kiralnih fosfinskih kompleksa Rh(I) u reakcijama katalitičkog enantioselektivnog hidrogeniranja

Saša Opačak, Zoran Kokan, Zoran Štefanić, Berislav Perić, Srećko I. Kirin

Institut Ruđer Bošković, Bijenička cesta 54, 10000 Zagreb
E-mail: Sasa.Opacak@irb.hr

Asymmetric catalysis is of crucial importance in science and industry. Traditionally, chiral induction in asymmetric catalysis is achieved by the vicinity of a chiral source and the reaction center. However, we have shown that chiral induction can also be achieved by a distant source of chirality; a maximal selectivity of 84 % *ee* was achieved by using aminoacid based phosphine ligands [1]. In our quest to increase the enantioselectivity we have shifted our attention from chiral aminoacids to chiral cyclic aliphatic diamines, since they are known to induce very high selectivity [2].

We have prepared a series of novel monodentate ligands comprised of three building blocks (Figure 1). The metal binding building block is a triphenylphospine with different substitution patterns: *para*-, *meta*- and *dimeta*-. The next building block is a disubstituted chiral diamine, cyclohexanediamine or cyclopentanediamine. Finally, the last building block has been designed to study the steric and electronic influence on selectivity in catalysis by incorporating different voluminous substituents or differently *para*-substituted benzoic acids. Rhodium complexes of the ligands were generated *in situ* and used as catalysts in asymmetric hydrogenation of model substrates, acetamidoacrylate **S1** and acetamido-cinnamate **S2**. The best result was achieved with the anthracene cyclohexanediamine *m*-phospine ligand which gave 91 % *ee* for **S1** and 96 % *ee* for **S2**. Further plans are to test our ligands on a wider range of model and commercially important substrates.

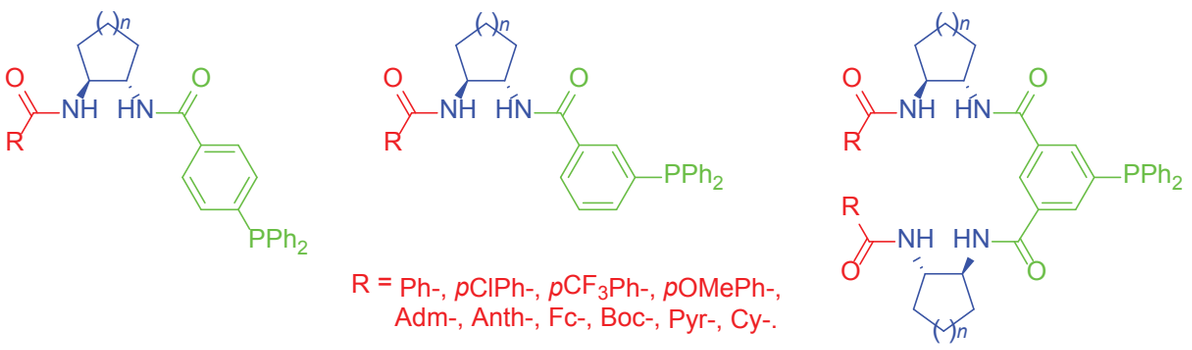


Figure 1: General ligand structure.

References

[1] Z. Kokan, Z. Glasovac, M. Majerić Elenkov, M. Gredičak, I. Jerić and S.I. Kirin, *Organometallics* **33** (2014) 4005-4015.

[2] B.M. Trost and M.L. Crawley, *Chem. Rev.* **103** (2003) 2921-2943.

STEREOCHEMISTRY OF HEXACOORDINATED TRANSITION METAL COMPLEXES WITH IMINODIACETAMIDE LIGANDS

Stereokemija heksakoordiniranih kompleksa prijelaznih metala s iminodiacetamidnim ligandima

Natalija P. Juraj,[1] Neven Smrečki,[2] Zora Popović,[2] Berislav Perić,[1] Srećko I. Kirin[1]

[1]*Division of Materials Chemistry, Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia*

[2]*Laboratory of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10000 Zagreb, Croatia*

E-mail: Natalija.Pantalon.Juraj@irb.hr

Hexacoordinated transition metal complexes of tridentate ligands **L** with $\mathbf{ML_2}$ stoichiometry can form several geometrical isomers: meridional, *trans*-facial, and delta or lambda *cis*-facial. The configuration of isomers is affected by steric and electronic properties of the ligands and coordinating ability of the counterions [1]. Derivatives of iminodiacetamide (imda) are studied as tridentate ligands and in all known complexes the iminodiacetamides act as O,N,O' chelators. The Cambridge Structural Database (CSD) contains crystallographic data for less than 20 metal complexes with iminodiacetamide or its *N*-substituted derivatives. All reported complexes of *N*-substituted imda derivatives are *trans*-facial isomers [2].

In this communication we present the synthesis and characterization of phenyl iminodiacetamide derivatives (**L1-L6**) and their $\mathbf{ML_2}$ complexes with transition metals, **M** = Zn(II), Co(II), Ni(II) or Cd(II). The amide nitrogen atoms were substituted with phenyl groups in order to increase their solubility in common organic solvents and enable characterization of complexes in solution. To test the effect of the ligands electronic properties on the complex configuration, ligands were prepared with electron donor or electron withdrawing groups on the *para*-position of phenyl rings (R). The complexes were characterized in solid state (single crystal X-ray diffraction, IR, TG) and in solution (^{1}H and ^{13}C NMR, IR, UV-Vis).

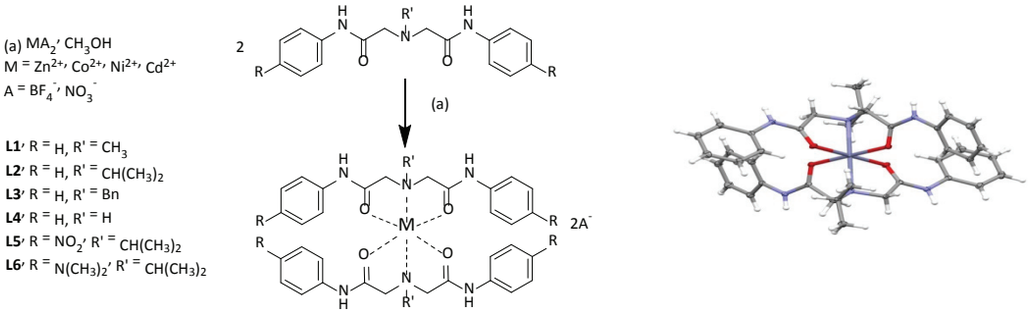


Figure 1: Synthesis of transition metal complexes (left) and crystal structure of *trans*-fac Zn(**L2**)$_2$ complex (right).

References

[1] Đ. Škalamera, E. Sanders, R. Vianello, A. Maršavelski, A. Pevec, I. Turel and S.I. Kirin, *Dalton Trans.* **45** (2016) 2845-2858.

[2] N. Smrečki, B.M. Kukovec, M. Đaković and Z. Popović, *Polyhedron* **93** (2015) 106-117.

CRYSTALLIZATION OF NEW COPPER HALIDE POLYMORPHS FROM SUPRAMOLECULAR GELS

Kristalizacija novih polimorfa bakrovih halogenida iz supramolekulskih gelova

Mario Cetina,[1] Zoran Džolić[2]

[1]*University of Zagreb, Faculty of Textile Technology, Department of Applied Chemistry, Prilaz baruna Filipovića 28a, HR-10000 Zagreb, Croatia*

[2]*Ruđer Bošković Institute, Bijenička c. 5, HR-10000 Zagreb, Croatia*
E-mail: mario.cetina@ttf.hr

The self-assembly of low-molecular-weight organogelators (LMWGs) renders supramolecular gels by the operation of hierarchical non-covalent forces. The unique features of supramolecular gels and their dynamic nature have stimulated numerous curiosity-driven studies, as well as the discovery of potentially innovative and highly technological applications. Particularly interesting is the exploitation of supramolecular gels as media for the crystal growth of molecular species since it is possible to attain different polymorphs and crystal habits, one of the key issue in pharmaceutical industry. Gel phase crystallization represents a *prime de facto* example of orthogonal self-assembly of the crystals and gel network, which are generally microphase separated and retain a distinct identity [1].

We have recently described the CuX_2-induced (X = Cl, Br) and water-mediated metallogel formation by a pyridine containing anthraquinone-based ligand in dimethyl sulfoxide (DMSO) [2]. This system withstands the presence of a significant excess of Cu(II) ions and we have exploited this unusual feature as a medium for a metal salt crystal growth. Indeed, the crystals of two copper halide polymorphs are produced spontaneously upon aging the Cu(II)-metallogel after one week at room temperature. X-ray crystal structure analysis *have shown* that one Cu(II) complex is mononuclear, while the other is dihalo-bridged Cu(II) complex. In both of them, $[CuBr_2(DMSO)_3]$ and $[CuCl(DMSO)_2(\mu\text{-}Cl)]_2$, polyhedron around the Cu(II) ion could be best described as distorted square pyramid (Figure 1).

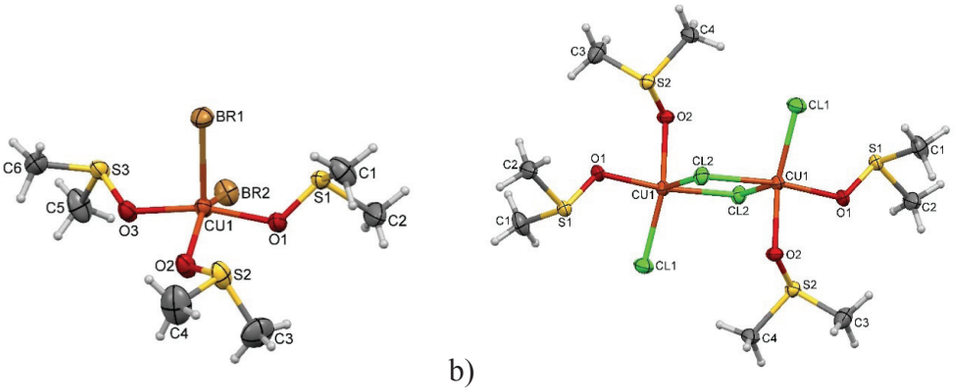


Figure 1: Molecular structures of $[CuBr_2(DMSO)_3]$ (a) and $[CuCl(DMSO)_2(\mu\text{-}Cl)]_2$ (b), with the atom numbering schemes. Displacement ellipsoids for non-hydrogen atoms are drawn at the 30 % probability level.

References

[1] D.K. Kumar and J.W. Steed, *Chem. Soc. Rev.* **43** (2014) 2080–2088.

[2] M. Cametti, M. Cetina and Z. Džolić, *Dalton Trans.* **44** (2015) 7223–7229.

DINUCLEAR FERROCENE DERIVATIVES AS A MODEL SYSTEM TO STUDY THE EFFECT OF VARIABLE SPACER LENGTH ON HYDROGEN BOND PATTERNS

Dinuklearni ferocenski derivati kao modelni sustav za proučavanje utjecaja različite duljine razmaknice na uzorke vodikovih veza

Ivan Kodrin,[1] Veronika Kovač,[2] Lidija Barišić,[2] Krešimir Molčanov[3]

[1]*Department of Chemistry, Faculty of Science, University of Zagreb, 10 000 Zagreb, Croatia*
[2]*Faculty of Food Technology and Biotechnology, University of Zagreb, Pierottijeva 6, 10 000 Zagreb, Croatia*
[3]*Department of Physical Chemistry, Ruđer Bošković Institute, Bijenička 54, 10 000 Zagreb, Croatia*
E-mail: ikodrin@chem.pmf.hr

Ferrocene-containing derivatives with only one ferrocene unit and two small peptide chains attached to each cyclopentadienyl ring show a great potential for formation of intra- or interchain hydrogen bonds because of a restricted rotation of these rings. An engagement of two ferrocene units imposes additional conformational flexibility in comparison to the mononuclear ferrocenes. The first oxalamide-bridged dinuclear ferrocene compound with acetyl groups did not show any preference for intramolecular hydrogen bonding [1]. In addition, these compounds did not exhibit any self-assembly and gelation properties, although some of the mononuclear ferrocene-containing and bis(amino acid)-oxalamide derivatives have already been proven as gelators [2,3].

If we want to predict the self-assembly and gelation properties of oxalamide-bridged dinuclear ferrocene peptides, firstly we need to fully understand the supramolecular structure and its relationship with molecular structure of single molecules. In order to make a clear distinction between affinities of potential hydrogen bond donor and acceptor sites toward inter- or intramolecular hydrogen bonding we performed a detailed conformational study by means of computational chemistry methods (DFT, QTAIM). The results were compared with those obtained by previously conducted experiments. In the course of this research, an improved procedure for syntheses of higher analogues of oxalamide-bridged dinuclear ferrocene compounds is described. In comparison with the first oxalamide-bridged compound [1] these analogues differ in spacer length and sizes of the oppositely attached peptide chains. The total number of potential hydrogen bond donor and acceptor sites increases in both compounds, thus resulting in the formation of multiple intramolecular hydrogen bonds. Nevertheless, some of these sites remain free and able to trigger unidirectional self-assembly and gelation behavior due to intermolecular hydrogen bonding.

References

[1] V. Kovač, K. Radošević, A. Bebek, J. Makarević, Z. Štefanić, L. Barišić, M. Žinić and V. Rapić, *Appl. Organometal. Chem.* (2016) 1–8.

[2] B. Adhikari, C. Singh, A. Shah, A. J. Lough and H.-B. Kraatz, *Chem. Eur. J.* **21** (2015) 11560–11572.

[3] L. Frkanec and M. Žinić, *Chem. Commun.* **46** (2010) 522–537.

Acknowledgments

This work was partially supported by the Croatian Science Foundation under the project HRZZ-IP-11-2013-7444.

SUPRAMOLECULAR ARCHITECTURES OF HALOGEN BONDED COCRYSTALS CONTAINING $CoCl_2L_2$ METAL-ORGANIC UNITS

Supramolekulska arhitektura kokristala povezanih halogenskom vezom koji sadrže $CoCl_2L_2$ metalo-organske jedinice

Katarina Lisac, Dominik Cinčić

Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, Zagreb, Croatia
E-mail: katarina.lisac@chem.pmf.hr

The assembly of metal-organic units is an attractive target for crystal engineering by halogen bonding, due to their potential to provide new magnetic, optical or electrical properties [1]. Herein we present $CoCl_2L_2$ complexes (L = 1,10 phenantroline, **phen**, or 2,2' bipyridine, **bpy**) as halogen bond acceptors and show their potential as building blocks for the construction of multicomponent materials by both liquid assisted grinding and conventional solution-based method. For cocrystal synthesis we selected commonly used, perfluorinated halogen bond donors: iodopentafluorobenzene (**ipfb**), 1,4-diiodotetrafluorobenzene (**14tfib**), 1,3-diiodotetrafluorobenzene (**13tfib**), 1,2-diiodotetrafluorobenzene (**12tfib**), 1,1,2,2,3,3,4,4-octafluoro-1,4-diiodobutane (**ofib**) and 1,3,5-trifluoro-2,4,6-triiodobenzene (**135tfib**). Single crystal X-ray diffraction experiments have shown that cocrystals display different supramolecular architectures governed by Cl···I halogen bonds between halogen bond donor iodine atoms and metal complex chlorine atoms (varying from 3.088 to 3.471 Å). Halogen bonded architectures in the cocrystal can be grouped into discrete molecular complexes (0D), chains (1D), two- and three-dimensional networks (2D and 3D). As expected, discrete complexes are formed using **ipfb,** a monotopic halogen bond donor, as well as **12tfib,** a ditopic donor. Halogen bonded chains were found in cocrystals with ditopic donors (**14tfib**, **13tfib**, **ofib**) as well as with **135tfib**, tritopic halogen bond donor. 2D and 3D networks are formed only using ditopic halogen bond donors **13tfib** and **ofib**. In all cocrystals halogen bonded aggregates are further connected by C-H···F, C-H···Cl, C-H···C, C-H···I, C-F···C, I···C or I···I contacts.

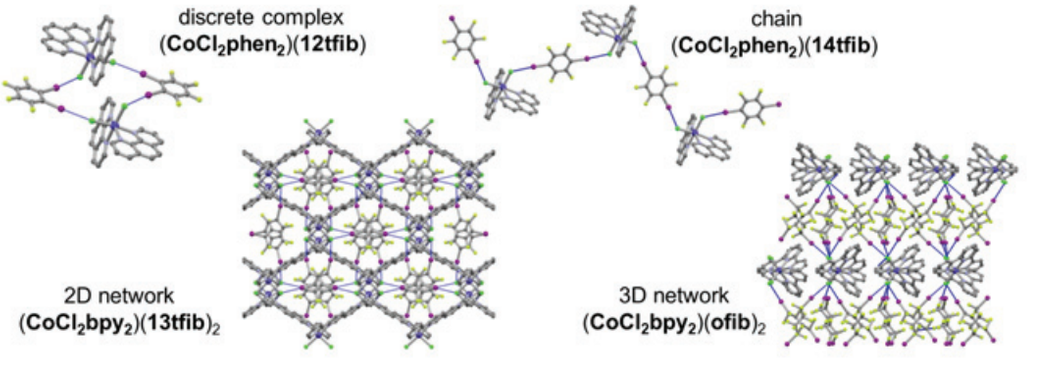


Figure 1: Examples of different supramolecular architectures in prepared $CoCl_2L_2$ cocrystals.

References

[1] R. Bertani, P. Sgarbossa, A. Venzo, F. Lelj, M. Amati, G. Resnati, T. Pilati, P. Metrangolo and G. Terraneo, *Coord. Chem. Rev.* **254** (2010) 677–695.

INTERACTIONS BETWEEN IODIDE IONS AND QUINOID RINGS

Interakcije između jodidnih iona i kinoidnih prstenova

Valentina Milašinović,[1] Krešimir Molčanov,[1] Vladimir Stilinović,[2] Gregor Mali,[3] Jože Grdadolnik[3]

[1]*Ruđer Bošković Institute, Bijenička 54, Zagreb HR-10000, Croatia*
[2]*Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, Zagreb HR-10000, Croatia*
[3]*National Institute of Chemistry, Hajdrihova 19, Ljubljana, SI-1000, Slovenia*
E-mail: valentina.milasinovic@irb.hr

A series of cocrystals of tetrachloro- and tetrabromoquinone with organic iodide salts has been prepared and structurally characterised. Derivatives *N*-methylpyridinium were chosen as cations, due to their planarity and similar size to the quinones, while their electronic properties are radically different. While the iodide usually acts as an electron donor, reducing the quinone into the semiquinone radical [1,2], sometimes the co-crystals of the neutral quinone and the iodide appear.

In the studied crystals, the common motive, or supramolecular synthon [3], has been identified: a sandwich-like I^-···quinone···I^- moiety with close contacts between the iodide anion and carbon skeleton of the quinoid ring (Fig. 1). Distances between the iodide and the ring centroid range between 3.6 and 3.85 Å, which is slightly shorter than sum of van der Waals radii for C and I. Interactions between π system aromatic ring and an anion are rarely observed, since aromatics are usually electron-rich; in the case of electron-depleted quinoid rings, anion···π contacts are more likely to form. In the studied cases, however, there is also a partial electron transfer between the iodide and the quinone which is noted by a change of colour: the neutral quinone is yellow, while the co-crystals and the semiquinone crystals are black.

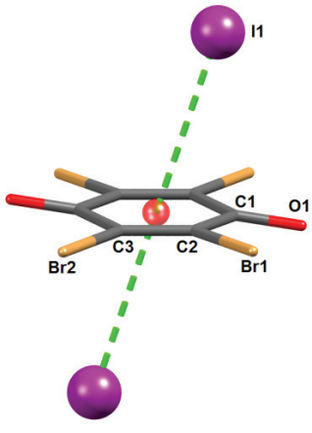


Figure 1: The I^-...quinone...I^- supramolecular synthon appearing in the studied structures.

References

[1] K. Molčanov, V. Stilinović, A. Šantić, N. Maltar-Strmečki, D. Pajić and B. Kojić-Prodić, *Cryst. Growth Des.* **16** (2016) 4777–4782.

[2] K. Molčanov, B. Kojić-Prodić, D. Babić, D. Pajić, N. Novosel and K. Zadro, *CrystEngComm* **14** (2012) 7958–7964.

[3] G.R. Desiraju, *Angew. Chem. Int. Ed.* **34** (1995) 2311–2327.

IMINES DERIVED FROM 2-HYDROXY-1-NAPHTHALDEHYDE AS HALOGEN BOND ACCEPTORS

Imini izvedeni iz 2-hidroksi-1-naftaldehida kao akceptori halogenske veze

Vinko Nemec, Dominik Cinčić

Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10000 Zagreb, Croatia
E-mail: vnemec@chem.pmf.hr

It has recently been shown that imines derived from *ortho*-vanillin and aromatic amines containing halogen bond acceptor moieties can form a variety of bonding motifs with halogen bond donors [1]. Since we have previously shown different bonding capabilities of select aromatic amines based on their substituent groups [2], our next goal was to investigate motif retention in a more robust building blocks. We synthesized a series of imines derived from 2-hydroxy-1-naphthaldehyde (**n**), and performed mechanochemical and solution cocrystallization experiments with 1,4-diiodotetrafluorobenzene (**tfib**). Eight aromatic amines have been selected for imine syntheses: 3-aminoacetophenone (**3aa**), 4-aminoacetophenone (**4aa**), 3-aminobenzonitrile (**3abn**), 4-aminobenzophenone (**4ab**), 4-aminobenzonitrile (**4abn**), 4-nitroaniline (**4noa**), 3-aminopyridine (**3ap**) and 5-amino-2-methoxypyridine (**5a2mp**).

Mechanochemical, powder X-ray diffraction and DSC experiments have shown that of our eight Schiff bases, only those with acetophenone or pyridyl fragments participate in cocrystal formation. Single crystal X-ray diffraction experiments have shown that, as expected [3], pyridine nitrogen atoms in the (**n3ap**)$_2$(**tfib**) cocrystal form strong halogen bonds with **tfib** (d(I···N) = 2.92 Å, ∠(C–I···N) = 175°). On the other hand, in the (**n5a2mp**)(**tfib**) cocrystal, halogen bonds are formed instead between **tfib** and methoxy oxygen groups (d(I···O) = 3.15 Å, ∠(C–I···O) = 167°) and between **tfib** and the π-system of the naphthaldehyde fragment (d(I···C) = 3.44 Å, ∠(C–I···C) = 166°).

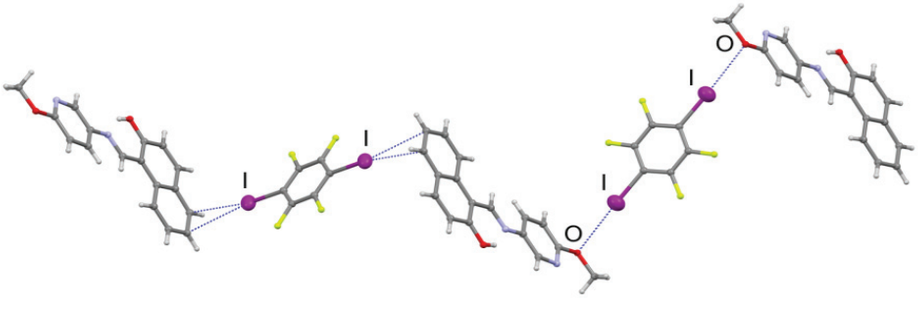


Figure 1: Part of the halogen bonded chain in the (**n5a2mp**)(**tfib**) cocrystal.

References

[1] M. Zbačnik, M. Vitković, V. Vulić, I. Nogalo and D. Cinčić, *Cryst. Growth Des.* **16** (2016) 6381–6389.

[2] V. Nemec and D. Cinčić, *CrystEngComm* **18** (2016) 7425–7429.

[3] G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimägi, G. Resnati and G. Terraneo, *Chem. Rev.* **116** (2016) 2478–2601.

COPPER(II) COMPLEXES WITH *N*-ARYLALKYLIMINODIACETAMIDE LIGANDS

Bakrovi(II) kompleksi s *N*-arilalkiliminodiacetamidnim ligandima

Zora Popović, Neven Smrečki, Vladimir Stilinović, Ozren Jović, Boris-Marko Kukovec

Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10000 Zagreb, Croatia
E-mail: zpopovic@chem.pmf.hr

The amide linkage is the most fundamental chemical bond in all proteins [1]. The binding of metal ions by amides, peptides and proteins is of great interest because of the importance of metal ions in biological systems [2]. Beside their obvious biological significance, amide ligands have many other valuable properties and many of them already found their practical application. They are used as pharmacological agents owing to their relatively good solubility and low toxicity. Amides also show potential for metal ion recognition. Furthermore, the amide moiety provides various possibilities of hydrogen bonding motifs which can be used to control the self-assembly processes between metal complexes in supramolecular coordination chemistry [3,4]. Recently, we discovered interesting supramolecular architectures in the structures of Cu(II) and Ni(II) complexes with *N*-arylalkyliminodiacetamides as hydrogen bond donors and nitrate ions as hydrogen bond acceptors [5,6]. In order to obtain similar architectures with other oxo-ions such as perchlorate ions (same charge, different symmetry) we synthesized a few novel copper complexes with *N*-arylalkyl derivatives of iminodiacetamide, namely $[Cu(Bnimda)_2](ClO_4)_2$ (**1**), $[Cu(Peimda)_2](ClO_4)_2$ (**2**) and $[Cu(Ppimda)_2](ClO_4)_2 \cdot 2H_2O$ (**3**) (Bnimda, Peimda, Ppimda; Bn = benzyl, Pe = 2-phenylethyl; Pp = 3-phenylprop-1-yl).

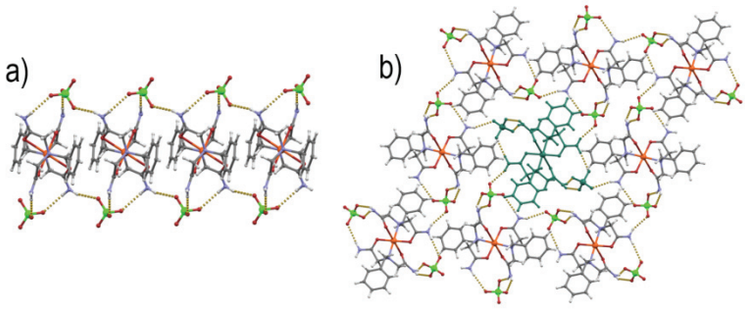


Figure 1: Crystal packing in **1.** a) Hydrogen bonded chains along the crystallographic *a* axis viewed along the crystallographic *b* axis; b) Interconnection of chains into a 3D structure viewed along the crystallographic *b* axis.

References

[1] J. M. Berg, J.L. Tymoczko and L. Stryer, *Biochemistry*, 5th ed., W.H. Freeman and Co., New York, 2002.

[2] W. Kaim and B. Schwederski, *Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life, Wiley, Chichester,* 1994.

[3] C. B. Aakeröy and A.M. Beatty, *Chem. Commun*. (1998) 1067–1068.

[4] J. M. Lehn, *Supramolecular chemistry – Concepts and perspectives*, VCH, Weinheim, 1995.

[5] N. Smrečki, B.-M. Kukovec, M. Đaković and Z. Popović, *Polyhedron* **93** (2015) 106–117.

[6] N. Smrečki, V. Stilinović, M. Merkaš, A. Lučić, B.-M. Kukovec and Z. Popović, *Aust. J. Chem*. **69** (2016) 896–904.

CHIRAL OXAMIDES AS HIGHLY EFFICIENT GELATORS FOR IONIC LIQUIDS

Kiralni oksamidi kao učinkoviti gelatori ionskih tekućina

Tomislav Portada, Ana Šantić, Andrea Moguš-Milanković, Leo Frkanec

Ruđer Bošković Institute, Zagreb, Croatia
E-mail: tomislav.portada@irb.hr

Chiral bis(amino acid and amino alcohol) oxamides belong to a class of efficient gelators of various organic solvents and water [1,2]. Their gelation ability is the result of unidirectional self-assembly into fibrous aggregates due to strong and directional intermolecular hydrogen bonding provided by oxamide units and the lack of molecular symmetry due to the presence of two chiral centers, which is known to prevent crystallization and favors aggregation. Additionally, bis(amino acid) oxamides show rather rare ambidextrous gelation behavior: they can gel both lipophilic, highly polar solvents and water due to their bolaamphiphilic structural features with well-separated lipophilic amino acid substituents and hydrophilic carboxylic acid or alcoholic OH groups located above and below the planar oxamide unit.

Recent study [3] showed that (*S,S*)-bis(leucinol)oxamide is highly efficient gelator for imidazole-based ionic liquid, capable of producing highly conductive supramolecular ionogel. This finding is very important since ionic liquids and materials based on ionic liquids are identified as "ideal" electrolytes for different applications due to their unique combination of properties such as negligible vapor pressure, non-flammability, chemical and thermal stability, high ionic conductivity, and wide electrochemical window.

In order to gain a deeper insight into the gelation properties of oxamide compounds towards ionic liquids we have expanded our survey to include gelation tests of series of amino-alcohol oxamides, namely ((*S,S*)-bis(leucinol)oxamide, (*S,S*)-bis(phenylalaninol) oxamide, (*S,S*)-bis(valinol) oxamide and (*S,S*)-bis(phenylglycinol)oxamide) and three ionic liquids, 1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylpyridine bis(trifluoromethylsulfonyl)imide and 1-butyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)imide. The results have shown that (*S,S*)-bis(valinol)oxamide is the most efficient gelator since it forms gel with all three ionic liquids, whereas bis(phenylglycinol)oxamide does not make gel with any of the tested ionic liquids. The minimum gelator concentration varies from $w = 0.3$ to 1.7 % indicating high gel-forming ability of the oxamide-based gelators. In addition, all prepared ionogels have very high ionic conductivity, comparable to those of the respective neat ionic liquid which classifies them to quasi-solid materials with a potential for application as novel electrolytes.

References

[1] L. Frkanec and M. Žinić, *Chem. Commun*. **46** (2010) 522–537.

[2] J. Makarević, M. Jokić, Z. Raza, Z. Štefanić, B. Kojić-Prodić and M. Žinić, *Chem. Eur. J.* **9** (2003) 5567–5580.

[3] A. Maršavelski, V. Smrečki, R. Vianello, M. Žinić, A. Moguš-Milanković and A. Šantić, *Chem. Eur. J.* **21** (2015) 12121–12128.

EFFECTS OF APPLICATION OF ULTRASONIC POWER ON THE CRYSTALLIZATION BEHAVIOR OF MALEATE SALT OF ACTIVE PHARMACEUTICAL INGREDIENT

Utjecaj ultrazvučnog zračenja na proces kristalizacije maleatne soli aktivne farmaceutske supstance

Martina Hrkovac,[1] Dejan Kišiček,[1] Damir Šahnić,[1] Eugen Marcelić,[1] Ernest Meštrović,[1]

[1]*PLIVA Croatia Ltd. (member of TEVA group), Prilaz baruna Filipovića 25, 10000, Zagreb, Croatia*
E-mail: Martina.Hrkovac@pliva.com

Simultaneous robust control of granulometric crystal properties (size, shape, size distribution) has become increasingly important in industrial practice [1] since it has an impact on filtration, residual moisture, downstream processes costs and, finally, bulk properties (density, flowability, compressibility)[2].

The maleate salt of active pharmaceutical ingredient (API) has characteristic very narrow metastable zone width (very close solubility and supersaturation curve) accompanied with lack of operating space for crystallization control. From a reason of very intensive nucleation, such conditions result with needle-like particles and broad size distribution. Since monitoring and control approaches can result in a better understanding of the process and significant improvement of product quality, process was monitored in real time by Focused Beam Reflectance Measurement (FBRM) instrument.

With a purpose to produce more uniform particles, the effect of continuous and pulsed ultrasonic treatment of different amplitudes and duration on the morphology of maleate salt of API was investigated. Suspension of the salt in appropriate solvent was prepared and was treated with the ultrasonic amplitudes of 30, 40, 50 and 60 % during 2.5 and 5 min. The difference in the quality of initial crystals and crystals obtained after ultrasonic irradiation is evident from the microscopic pictures of the product obtained from each experiment. The increasing the ultrasonic time exposure of the particles (5 min instead 2.5 min) resulted with no significant change in particle size distribution.

Furthermore, on the basis of good morphological results obtained with sonocrystallization and the fact that the metastable zone width is very narrow and unvafourable, the influence of the ultrasound irradiation at the nucleation point and during crystallization process of maleate salt of API was investigated. It was found that ultrasonic waves directly influence the morphology of the maleate salt of the API during crystallization process and product of a better and improved quality was manufactured.

This work shows important research developments and arising challenges in the field of industrial crystallization.

References

[1] Z.K. Nagy and R.D. Braatz, *Annu. Rev. Chem. Biomol. Eng.* **3** (2012) 55-75.

[2] J. Garside, A. Mersmann and J. Nyvlt, *Measurement of Crystal Growth and Nucleation Rates*, IChem^{E}, Rugby, 1989.

DIRECT NUCLEATION CONTROL OF FUMARATE SALT OF API USING FBRM AND SPECTROSCOPIC METHODS

Direktna kontrola nukleacije fumaratne soli API-a pomoću FBRM-a i spektroskopskih metoda

Dejan Kišiček, Martina Hrkovac, Damir Šahnić, Eugen Marcelić, Ernest Meštrović

PLIVA Hrvatska d.o.o., TAPI Research & Development, Zagreb, Croatia
E-mail: dejan.kisicek@pliva.com

Particle size is a crucial characteristic of the active pharmaceutical ingredient (API), and particle size distributions (PSD) are an important consideration for pharmaceutical manufacturers [1]. PSDs, the range of the individual particle sizes that make up a substance, should be narrow, so that most individual particles fall within a specific, tightly defined size range. The PSDs of API may influence key performance factors such as bioavailability, dissolution, stability, uniformity of content, etc. [2].

Optimization of the crystallization process of fumarate salt of the API using Focused Beam Reflectance Measurement (FBRM) technology and analytical methods such as Raman and ATR-UV/Vis spectroscopy is described and discussed. FBRM is used as in-line analytical method for observing particle size and counts of particles in the suspension in real time. Spectroscopic methods were used to observe concentration of API in solution during crystallization process to determine supersaturation level in order to define optimal conditions for crystallization control. That approach has resulted in gaining larger particles referring to d_{90} parameter and narrower PSD. A crystallization of fumarate salt of API in *n*-butanol shows all the benefits of a combination of the FBRM probe with various analytical methods during crystallization process. Characterizing particle properties effectively, in particular mean particle size and particle size distribution, allows processing problems to be solved and product quality to be improved.

References

[1] Alan M. Marks, John J. Sciarra, *Journal of Pharmaceutical Science,* **57** (1968) 497–504.

[2] Anthony J. Hlinak, Kamal Kuriyan, Kenneth R. Morris, Gintaras V. Reklaitis, and Prabir K. Basu. *Journal of Pharmaceutical innovation* **1** (2016)12-17.

PREPARATION AND CHARACTERIZATION OF AMORPHOUS MATERIAL OBTAINED *VIA* SPRAY DRYING TECHNOLOGY

Priprava i karakterizacija amorfnog materijala dobivenog sušenjem raspršivanjem

Igor Nežić,[1] Aleksandra Sander,[2] Ernest Meštrović [1]

[1]*PLIVA Croatia LTD, Zagreb, Croatia*

[2]*Faculty of Chemical Engineering and Technology, Zagreb, Croatia*
E-mail: igor.nezic@pliva.com

Drying is perhaps the oldest, most common and most diverse of chemical engineering unit operations. Over four hundred types of dryers have been reported in the literature while over one hundred distinct types are commonly available. [1] Spray drying, amongst other technologies, is a well-established technology for the production of amorphous products. It offers the possibility to modify powder characteristics such as particle size, particle morphology, crystallinity and the amount of residual solvent. [2]

In this work, 5-(4-(4-(5-Cyano-1H-indol-3-yl)butyl)piperazin-1-yl)benzofuran-2-carboxamide hydrochloride (Figure 1) was used as a model molecule for preparation and characterization of stable amorphous form of the active pharmaceutical ingredient by means of spray dryer technology. For the purpose of feed solution preparation, solubility of crystalline structure was determined in variety of pure solvents as well as mixture of solvents and most suitable system was chosen. Feed solution of the active pharmaceutical ingredient, dissolved in mixture of acetonitrile and water, was dried at different process conditions such as inlet temperature, nitrogen flow rate used for atomization and feed solution flow rate. The influence of process conditions on physical and chemical properties of final dried product was examined on a variety of analytical and physical methods. The results showed that a stable amorphous structure of the high purity active pharmaceutical ingredient is obtained with a spray drying, and that the optimal conditions of the process are defined. The amorphous structure is stable at temperatures below 200 °C when it is transformed into a new crystal structure. Conditions of high relative air humidity lead to partial transformation.

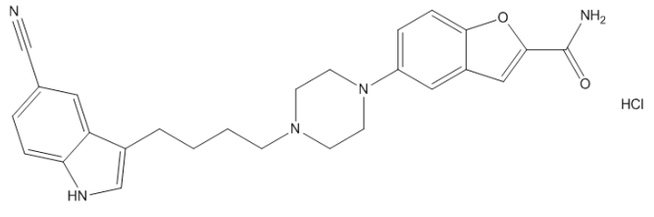


Figure 1: Structure of 5-(4-(4-(5-Cyano-1H-indol-3-yl)butyl)piperazin-1-yl)benzofuran-2-carboxamide hydrochloride.

References

[1] A.S. Mujumdar, *Guide to industrial drying: principles, equipment and new developments,* Colour Publications, Mumbai, 2004.

[2] P. Thybo, L. Hovgaard, J.S. Lindeløv, A. Brask, S.K. Andersen, *Scaling Up the Spray Drying Process from Pilot to Production Scale Using an Atomized Droplet Size Criterion,* Pharmaceutical Research, **25 (7)** (2008) 1610-1620.

BIOSORPTION AND BIODEGRADATION OF CARBON COMPOUNDS FROM PHARMACEUTICAL INDUSTRIAL WASTEWATER

Biosorpcija i biorazgradnja ugljikovih spojeva iz farmaceutske industrijske otpadne vode

Monika Šabić,[1] Nikolina Janton,[1] Marija Vuković Domanovac,[1] Ernest Meštrović[2]

[1]*Department of Industrial Ecology, Faculty of Chemical Engineering and Technology,*

University of Zagreb, Marulićev trg 19, HR-10 000 Zagreb

[2]*PLIVA Croatia d.o.o., Prilaz baruna Filipovića 25, HR-10 000 Zagreb*

E-mail: msabic@fkit.hr

Biological wastewater treatment with activated sludge is commonly used technology for contaminants removal from wastewater. It has significant efficiency and decreases ecological footprint. Activated sludge consists primarily of bacteria which are connected in activated sludge flocs. Its main role is the removal of carbon compounds from wastewater with biosorption and biodegradation. Biosorption is a process where carbon compounds from wastewater are attached on the surface of biomass cell structure or accumulated within the structure of a floc [1]. Microorganisms from activated sludge can metabolize captured carbon compounds to the final main products, carbon dioxide and water. In this way biodegradation becomes the substantial process for the removal of organic contaminants [2].

The aim of this work was to study biosorption and biodegradation of organic contaminants from pharmaceutical industrial wastewater with activated sludge. The experiments were conducted in batch conditions with initial concentration of pharmaceutical wastewater, $S_0 = 5473 \pm 85.6$ mg dm^{-3}, and different initial concentrations of activated sludge, which ranged between 2.82 and 5.98 g dm^{-3}. During the experiments, chemical oxygen demand (COD), concentration of biomass, dissolved oxygen and pH-value were monitored. Microscopic analysis was also conducted. In biosorption, the equilibrium was reached within 30 minutes and process efficiency was 20.5 %. Biodegradation process was described with Endo-Haldane model. Biokinetic parameters were estimated to be $\mu_{max} = 0.19$ h^{-1}, $K_S = 113.09$ g dm^{-3}, $K_i = 8.05$ g dm^{-3}, $k_d = 4.23 \cdot 10^{-3}$ h^{-1} and $Y = 0.19$ g g^{-1}. Overall efficiency of biodegradation process was 74.4 %.

References

[1] C.-P. Lim, J.L. Neo, E. Mar'atusalihat, Y. Zhou, W.J. Ng, *Biochemical Engineering Journal* **114** (2016) 119-129.

[2] I. Martínez-Alcalá, J. M. Guillén-Navarro, C. Fernández-López, *Chemical Engineering Journal* **316** (2017) 332-340.

THE INFLUENCE OF AMINO ACIDS RELEVANT FOR PATHOLOGICAL BIOMINERALIZATION ON THE PRECIPITATION OF CALCIUM OXALATE MONOHYDRATE

Utjecaj aminokiselina relevantnih za patološku biomineralizaciju na taloženje kalcijeva oksalata monohidrata

Anamarija Stanković,[1] Jasminka Kontrec,[2] Branka Njegić Džakula,[2] Nadica Maltar Strmečki,[2] Daniel Mark Lyons,[2] Berislav Marković,[1] Damir Kralj[2]

[1]*Department of Chemistry, J. J. Strossmayer University of Osijek, Osijek, Croatia*

[2]*Ruđer Bošković Institute, Zagreb, Croatia*
E-mail: bmarkovi@kemija.unios.hr

Urolithiasis, a form of pathologic biomineralization, is a disease which causes the formation of urinary stones in different parts of kidney or bladder [1]. Recently, increasing number of kidney stones in industrial countries is observed and the interest of scientists to explain their pathogenesis with a special focus on calcium oxalate stones is renewed. Calcium oxalates crystallize in the form of hydrated salts: thermodynamically stable calcium oxalate monohydrate (COM, $CaC_2O_4 \cdot H_2O$, whevellite) [2,3] and metastable dehydrate (COD, $CaC_2O_4 \cdot 2H_2O$, weddellite) [4,5], and trihydrate (COT, $CaC_2O_4 \cdot 3H_2O$) [6,7]. The kidney stones formation under biological conditions can be triggered by various metabolic disorders such as: hipercalciuria, hypocitraturia, hiperoxaluria, and the change in the urine acidity. The mechanisms and the conditions under which they crystallize are still not completely clarified.

In this work, the spontaneous precipitation and characterization of calcium oxalate monohydrate under conditions of hiperoxaluria is reported. The experiments were conducted in a simple model system and with the addition of amino acids reportedly important for pathologic biomineralization [8,9]. The precipitations were carried out with solutions $c_i(Ca^{2+}) = 7.5 \times 10^{-3}$ mol dm^{-3} and $c_i(C_2O_4^{2-}) = 6.0 \times 10^{-3}$ mol dm^{-3}. The amino acids selected for the addition are often found in the urine of healthy people and in the organic matrix which is an integral part of kidney stones.

The reactant solutions were mixed under controlled hydrodynamic and thermodynamic conditions. Changes in the composition and morphology of precipitated calcium oxalate monohydrate were observed by means of PXRD, EPR, SEM, IR and TGA.

References

[1] B. Hess, R.L.R., J. Kavanagh, S.R. Khan, D.J. Kok, A.L. Rodgers and H.G Tiselius, *Eur. Urol.* **40** (2001) 220-230.

[2] Lj. Brečević and D. Kralj, *J. Cryst. Growth* **79** (1986) 178-184.

[3] Lj. Brečević, D. Kralj and J. Garside, *J. Cryst. Growth* **97** (1989) 460-468.

[4] C. Conti, M. Casati, C. Colombo, M. Realini, L. Brambilla and G. Zerbi, *Spectrochim. Acta A* **128** (2014) 413-419.

[5] P. Brown, D. Ackermann and B. Finlayson, *J. Cryst. Growth* **98** (1989) 285-292.

[6] D. Škrtić, M. Marković, Lj. Komunjer and H. Füredi-Milhofer, *J. Cryst. Growth* **66** (1984) 431-440.

[7] D. Škrtić, H. Füredi-Milhofer and M. Marković, *J. Cryst. Growth* **80** (1987) 113-120.

[8] K. Kohri, M. Takada, Y. Katoh, K. Kataoka, M. Iguchi and T. Kurita, *Int. Urol. Nephr.* **21** (1989) 9-16.

[9] S.S. Atanassova, P. Panchev and M. Ivanova, *Amino Acids* **38** (2010) 1277-1282.

RADIOLYTICAL SYNTHESIS OF IRON OXIDE NANOPARTICLES IN THE PRESENCE OF PEO, PVP, CTAB AND DEAE-DEXTRAN

Radiolitička sinteza nanočestica željezovih oksida u prisutnosti PEO-a, PVP-a, CTAB-a i DEAE-dekstrana

Tanja Jurkin,[1] Marijan Gotić[2], Goran Štefanić,[2] Irina Pucić[1]

[1]*Radiation Chemistry and Dosimetry Laboratory, Division of Materials Chemistry, Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia*

[2]*Center of Excellence for Advanced Materials and Sensing Devices, Research Unit New Functional Materials, Ruđer Bošković Institute, Bijenička 54, Zagreb, Croatia*
E-mail: tjurkin@irb.hr

Magnetic iron oxide nanoparticles (NPs) have applications as sensor, as contrast agents for MR imaging, in drug delivery and for hyperthermia cancer treatments. γ-irradiation is a powerful technique to synthesize NPs of controlled size and shape in solution, with advantage of inducing solvated electrons and radicals, able to reduce metal ions, homogeneously through the sample. The use of polymers or surfactants can influence the nanoparticle size, morphology, stability and dispersivity. The goal of this work was to study the influence of selected polymers/surfactant on the radiolytical synthesis of iron oxides. Iron(III) precursor solutions were γ-irradiated in the presence of poly(ethylene oxide) (PEO), polyvinylpyrrolidone (PVP), cetyltrimethylammonium bromide (CTAB) and diethylaminoethyl-dextran hydrochloride (DEAE-dextran) [1]. γ-irradiation of iron(III) chloride/PEO aqueous solution produced rigid PEO hydrogels with embedded iron oxide NPs (Fig. 1a). Addition of 2-propanol increased the reducing power of γ-irradiation resulting in the formation of magnetite NPs (Fig. 1b); however 2-propanol reduced PEO crosslinking and thus less rigid hydrogels or suspensions were formed. PVP in Fe(III) solution produced magnetic suspension with a small amount of δ-FeOOH (feroxyhyte). γ-irradiation of Fe(III)/CTAB aq. solution favoured the formation of rod-like goethite NPs (Fig. 1c). Surprisingly, γ-irradiation of Fe(III)/DEAE-dextran aq. solution with 2-propanol produced almost pure δ-FeOOH magnetic nanodiscs (Fig. 1d). This result present the first report of γ-irradiation synthesis of δ-FeOOH and the first report of obtaining δ-FeOOH in nanodisc morphology [2].

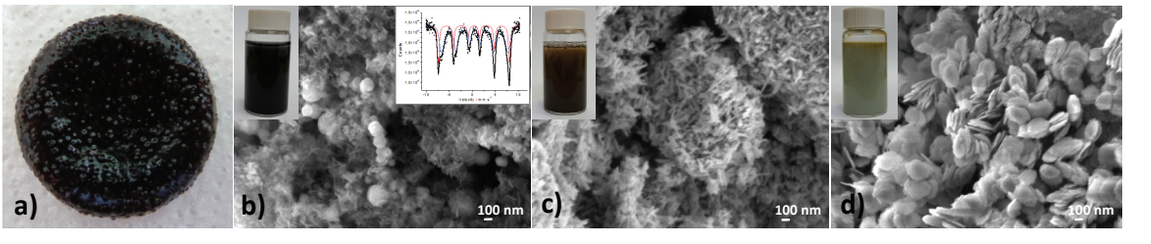


Figure 1: SEM images, photos and Mössbauer spectrum of different iron oxide nanoparticles and composite gel prepared by γ-irradiation of Fe^{3+} aqueous solutions in the presence of PEO (a, b), CTAB (c) and DEAE-dextran (d). Nanocomposite gel (a); magnetite NPs (b); rod-like goethite NPs (c); δ-FeOOH magnetic nanodiscs (d).

References

[1] T. Jurkin, M. Gotić, G. Štefanić and I. Pucić, *Radiat. Phys. Chem.* **124** (2016) 75-83.

[2] T. Jurkin, G. Štefanić, G. Dražić and M. Gotić, *Mater. Lett.* **173** (2016) 55-59.

CORRELATION BETWEEN MOLECULE GEOMETRY AND FORMATION OF SPONTANEOUSLY CHIRAL *TWIST-BEND* NEMATIC PHASE

Ovisnost nastanka spontano kiralne *twist-bend* nematičke faze o geometriji molekula

Andreja Lesac[1], Ute Baumeister[2], Irena Dokli[1], Zdenko Hameršak[1], Trpimir Ivšić[1], Darko Kontrec[1], Marko Viskić[1], Anamarija Knežević[1]

[1]*Ruđer Bošković Institute, Zagreb, Croatia*

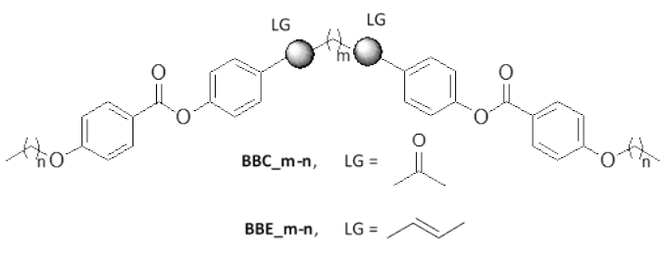
[2]*Institute of Chemistry, Martin Luther University Halle-Wittenberg, Halle, Germany*

E-mail: Anamarija.Knezevic@irb.hr

Since the *twist-bend* nematic phase (N_{TB}) has been predicted for bent-shaped molecules [1], a series of studies reported the evidence of chiral molecular organization within the N_{TB} phase. This chiral organization is consistent with an oblique helicoidal structure and is obtained even when the molecules are achiral. Despite an effort to determine how variations in molecular structure affect incidence of the N_{TB} phase, a general and comprehensive relationship between molecular structure and the formation of the N_{TB} phase is still elusive [2,3].

Herein we report a comprehensive study, which includes synthesis, mesomorphic properties and molecular modeling, of novel carbonyl- or ethenyl- linked symmetric dimers (Figure 1.a). These new sets of dimers primary differ in the nature of linkage group. Transition properties for ethenyl-linked dimers show that all compounds display both the uniaxial nematic and N_{TB} phase. In contrast to ethenyl series, the N_{TB} phase was observed only in the homologues with the shortest terminal chains, regardless the spacer length.

The comparison of mesomorphic properties of these two series complemented with computational studies of conformational space around the linkage group revealed that intramolecular torsion in conjunction with molecular curvature plays an important role in formation of a spontaneously chiral twist-bend nematic phase. (Figure 1.b).



a)

b)

Figure 1: a) The structure of novel symmetric ethenyl BBE_m-n and carbonyl linked BBC_m-n dimers; b) POM rope texture of the N_{TB} phase of BBE_7-2 at 98 °C

References

[1] I. Dozov, *Europhys. Lett. EPL* **56** (2001) 247–253.

[2] R. J. Mandle, *Soft Matter* **12** (2016) 7883–7901.

[3] T. Ivšić, U. Baumeister, I. Dokli, A. Mikleušević, A. Lesac, *Liq. Cryst.* (2016) 1–13.

SYNTHESIS OF UNIFORM PLATE-LIKE {001} CALCITE CRYSTAL SEED

Sinteza uniformnog pločastog {001} kalcitnog kristalnog sjemena

Nives Matijaković,[1] Michela Reggi,[2] Giuseppe Falini[2] and Damir Kralj[1]

[1]*Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia*

[2]*Department of Chemistry, University of Bologna, Via Zamboni 33, 40126 Bologna, Italy*

E-mail: nmatijak@irb.hr

Calcium carbonate crystals are interesting model for studying the additive-controlled processes that are important for pharmaceutical industry and for understanding the crystallization in biological systems [1]. Calcite, the most stable calcium carbonate polymorph, can crystallize with notable variety of habits under different environmental conditions. Indeed, it is known that the addition of inorganic ions such as Mg^{2+}, SO_4^{2-} or Li^+ can exert profound effect on the morphology of calcite precipitated in aqueous systems [2]. Previously, it has been shown that increasing amounts of lithium ions enhance the formation of {001} calcite form [3]. Such crystals could be used as a good model for determination of adsorption mechanisms of organic molecules on the {001} calcite surface.

The aim of this study was to prepare the plate-like and uniform calcite crystal seed, with well-developed {001} faces. For that purposes, the influence of the lithium ions concentration, in the range from $c = 0$ to 1.0 mol dm^{-3} and a mode of agitation have been systematically studied as a critical parameter of this specific $CaCO_3$ precipitation process. Calcite samples were characterized by means of FTIR/ATR spectroscopy and PXRD. In addition, the SEM and AFM microscopy were used for identification and surface analysis of {001} faces, while the chemical composition of the precipitate has been determined by the ion chromatography. The results have indicated that the addition of lithium ions has a significant influence on the polymorphic composition, as well as on the morphology of calcite crystals. It has been shown that the uniform plate-like calcite is preferably precipitated after the addition of Li^+ at concentration $c = 0.3$ mol dm^{-3}.

References

[1] S. Raman, S. Mann, *J. Chem. Soc., Chem. Commun.*, **24** (1990) 1789-1791.

[2] L. Wang, E. Ruiz-Agudo, C. V. Putnis, A. Putnis, *Cryst. Eng. Comm*., **13** (2011) 3962-3966.

[3] D. Aquilano, L. Pastero, *Cryst. Res. Technol*., **48** (2013) 819-839.

ION-POLARON CHARGE TRANSPORT IN ALKALI ZINC PHOSPHATE GLASSES CONTAINING WO_3 AND MoO_3

Prijenos naboja kod ionsko-polaronskih alkalijskih cinkovih fosfatnih stakala koja sadrže WO_3 i MoO_3

Juraj Nikolić,[1] Ana Šantić,[1] Petr Mošner,[2] Ladislav Koudelka,[2] Andrea Moguš-Milanković[1]

[1]*Department of Materials Chemistry, Ruđer Bošković Institute, 10000 Zagreb, Croatia*

[2]*Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, 53210 Pardubice, Czech Republic*

E-mail: jnikolic@irb.hr

Glass systems of the composition $(30–0.5x)M_2O–(30–0.5x)ZnO–40P_2O_5–xTMO$ ($0 \leq x \leq 60$ mol. %) were studied (M = Na, Li; TMO = WO_3, MoO_3). These glasses show interesting electrical properties due to potential coexistance of two different conduction mechanisms. Generally, at high alkali metal oxide content ionic conduction is predominant whereas at high transition metal oxide content polaronic conduction is preferred. In glasses with equal content of both alkali and transition metal oxide a conductivity minimum should be observed. This effect is known as ion-polaron effect and it has been a subject of investigation for decades. [1]

Structure of glasses was investigated by Raman and infrared spectroscopy (IR). Glasses with high alkali metal oxide content contain mostly metaphosphate units (Q^2) which depolymerize with the addition of TMO. Also, in these glasses, at very high content of TMO, the TMO starts acting as both network modifier and network former. [2,3]

Electrical and dielectric properties of glasses have been studied by impedance spectroscopy in wide frequency and temperature ranges. The results have shown that these glasses show a minimum of conductivity with increasing TMO content. Conductivity minimum in all series of glasses suggest that the coupling of ionic and polaronic conduction mechanisms occur which can be attributed to ion-polaron effect.

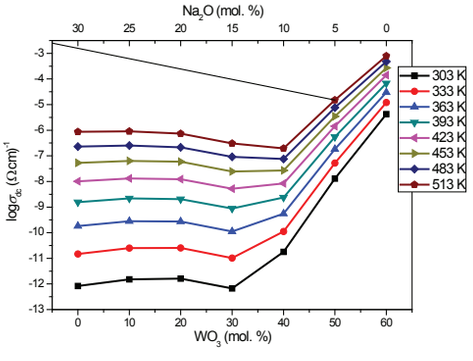


Figure 1: DC conductivity trend of sodium-tungsten series.

References

[1] J. C. Bazan, J. A. Duffy, M. D. Ingram, M. R. Mallace, *Solid State Ionics* **86-88** (1996) 497-501.

[2] J. Šubčík, L. Koudelka, P. Mošner, L. Montagne, G. Tricot, L. Delevoye, I. Gregora, *J. Non-Cryst. Solids* **356** (2010) 2509-2516.

[3] L. Koudelka, J. Šubčík, P. Mošner, *Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B* **53** (2012) 79-85.

ELECTRICAL TRANSPORT IN IRON (BORO)PHOSPHATE GLASSES CONTAINING HfO_2 AND CeO_2

Električni transport u željeznim (boro)fosfatnim staklima s HfO_2 i CeO_2

Luka Pavić,[1] Ana Šantić,[1] Radha D. Banhatti,[1] Mevlut Karabulut,[2] Andrea Moguš-Milanković[1]

[1]*Division of Materials Chemistry, Ruđer Bošković Institute, 10000 Zagreb, Croatia*

[2]*Physics Department, Faculty of Science, Gebze Technical University, 41400 Gebze, Turkey*

E-mail: lpavic@irb.hr

Phosphate glasses containing transition metal oxide such as Fe_2O_3 exhibit polaronic conductivity as a result of electron hopping from Fe^{2+} to Fe^{3+} ions, which is described by *small polaron hopping* model. The electrical and dielectric properties of three series of glasses (11 samples), HfO_2-Fe_2O_3–P_2O_5, CeO_2-Fe_2O_3–P_2O_5, and HfO_2-Fe_2O_3-B_2O_3–P_2O_5, were investigated using impedance spectroscopy over a wide frequency (0.01 Hz–1 MHz) and temperature range (303-513 K), whereas fraction of ferrous ions was determined by Mössbauer spectroscopy. Detailed analysis of conductivity and permittivity spectra was done to gain a better insight into factors that possibly influence polaron transport.

In all three glass systems with wide variation of Fe^{2+} content a maximum in conductivity is observed at slightly below $Fe^{2+}/Fe_{tot} \approx 0.5$ which confirms that electrical transport is strongly controlled by polaron concentration via fraction of ferrous ions, Fe^{2+}/Fe_{total}, and overall Fe_2O_3 content. Conductivity spectra for all glasses were analyzed in the model-free approach with various scaling procedures and in addition were also modelled with MIGRATION concept. It is found that in each series of glasses the shape parameter describing conductivity dispersion remains the same indicating that the mechanism of conductivity is unchanged. Sidebottom scaling of conductivity spectra which takes into account experimental dielectric strength parameter showed that it is possible to obtain super-master curve, whereas with Summerfield scaling additional shift is required on the frequency axis. Observed feature implies that for all our systems not only does the charge carrier concentration change with composition, but also the typical length of a polaron hop. Furthermore, characteristic spatial extent of localized hopping of polarons is calculated from scaled experimental permittivity spectra and it shows a decreasing trend with increasing polaron concentration. Obtained values lie in the range of values for polaron radius calculated from equation proposed by Bogomolov.

This study has revealed that electrical transport in these polaronic glasses is, in addition to polaron concentration, also influenced by polaronic hopping distance which is changing with composition due to an alteration in distribution of iron ions in the glass matrix.

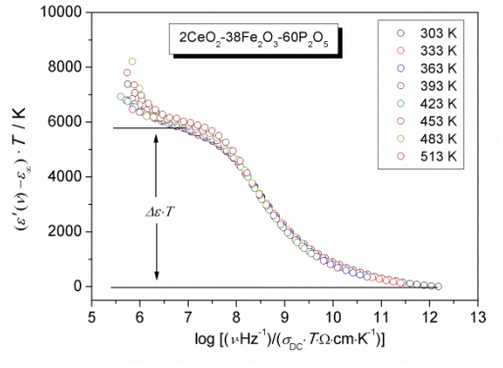


Figure 1: Scaled permittivity spectra of the $2CeO_2$–$38Fe_2O_3$–$60P_2O_5$ glass using Summerfield procedure.

MORPHOLOGY, INTERFACIAL AND MECHANICAL PROPERTIES STUDY OF *SILICA* REINFORCED iPP/SEBS(-*g*-MA) COMPOSITES

Istraživanje morfologije, međupovršinskih i mehaničkih svojstava iPP/SEBS(-*g*-MA) kompozita ojačanih *silikom*

Anđela Pustak,[1] Matjaž Denac,[2] Mirela Leskovac[3], Iztok Švab[4], Vojko Musil[2], Ivan Šmit[1]

[1]*Ruđer Bošković Institute, Division of Materials Chemistry, Zagreb, Croatia*

[2]*University of Maribor, FEB Maribor, Institute of Technology, Maribor, Slovenia*

[3]*University of Zagreb, Faculty of Chemical Engineering and Technology, Zagreb, Croatia*

[4]*ISOKON, Production and Processing of Thermoplastics, Ltd, Slovenske Konjice, Slovenia*

E-mail: apustak@irb.hr

The effects of different silica and elastomeric content on morphology, interfacial properties, and mechanical properties of polypropylene/silica 96/4 composites modified with 5, 10, 15, and 20 vol% of poly(styrene-*b*-ethylene-*co*-butylene-*b*-styrene) SEBS and SEBS grafted with maleic acid (SEBS-*g*-MA) were investigated. Four silica fillers differing in size (nano- *vs.* micro-) and in surface properties (untreated *vs.* treated) were chosen as fillers. Elastomers SEBS and SEBS-*g*-MA were added as impact modifier and compatibilizer at the same time.

The morphology of binary blends and ternary polymer composites was studied by different microscopy techniques. While in binary iPP/SEBS(-*g*-MA) blends prevails typical two phase morphology with iPP as matrix, the ternary composites revealed the wide spectrum of morphologies rather than one exclusive, depended primarily on interfacial properties. [1,2]

Both iPP/silica/SEBS(-*g*-MA) composites preferred compartmentalized morphology (as the variety of core-shell m.) with hydrophilic silica while with hydrophobic silica there is a wide spectrum of different morphologies. The spherulitic morphology of polypropylene matrix in iPP/silica/SEBS(-*g*-MA) composites was abrupt with the addition of silica and the final morphology was a result of two competitive effects: nucleation effect of filler and solidification effect of elastomer. Tensile and impact strength properties were mainly influenced by combined competitive effects of stiff filler and tough SEBS(-*g*-MA) elastomer. Both elastomers showed great impact modifying properties.

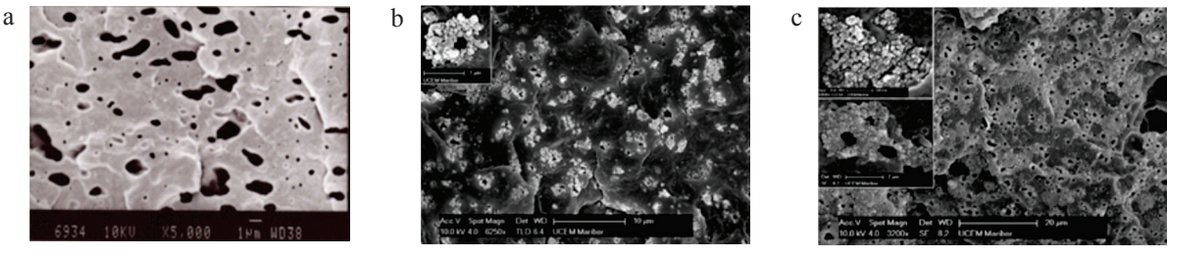


Figure 1: a) SEM pictures showing different morphologies: iPP/SEBS binary blend 80/20; b) iPP/silica 96/4 + 20% SEBS; c) iPP/silica 96/4 + 20% SEBS-g-MA

References

[1] A. Pustak, M. Denac, M. Leskovac, I. Švab, V. Musil, I. Šmit, *Journal of Applied Polymer Science* **132** (2015) 41486-41498.

[2] A. Pustak, M. Denac, M. Leskovac, I. Švab, V. Musil, I. Šmit, *Polymer-Plastic Technology and Engineering* **54** (2015) 647-660.

HETEROPOLYNUCLEAR COMPOUNDS CONTAINING $[Cu(L)(\mu\text{-}C_2O_4)Cu(L)]^{2+}$ UNITS BRIDGED BY $[Cr(C_2O_4)_3]^{3-}$ OR $Cr_2O_7^{2-}$: A VARIETY OF UNUSUAL COORDINATION MODES

Heteropolinuklearni spojevi s jedinkama $[Cu(L)(\mu\text{-}C_2O_4)Cu(L)]^{2+}$ premoštenim s $[Cr(C_2O_4)_3]^{3-}$ odnosno $Cr_2O_7^{2-}$: niz neobičnih načina koordiniranja

Lidija Kanižaj, Krešimir Molčanov, Marijana Jurić

Ruđer Bošković Institute, Bijenička cesta 54, Zagreb, Croatia
E-mail: Lidija.Kanizaj@irb.hr

Heteropolynuclear metal complexes have been widely investigated for their ability to form different architectures and topologies, and also due to their interest for applications in catalysis, photoluminescence, gas storage and separation, magnetism and multifunctional molecular materials. In the last few decades, the chemistry of oxalate-containing complexes has become an active area of research – the oxalate moiety, $C_2O_4^{2-}$, acts as a linker between metal centres with various possibilities of bridiging modes. It is particularly interesting due to its ability to mediate electronic effects between paramagnetic metal ions. Stable mononuclear anionic oxalate complexes are often used as ligands toward another metal ion. The use of the $[Cr(C_2O_4)_3]^{3-}$ anion in the reactions with organic and inorganic cations results in different structure types, from discrete polynuclear metal compounds to polymeric one- (1D), two- (2D) or threedimensional (3D) assemblies, featuring a range of distinct magnetic properties.

Applying the layering technique i.e. slow liquid diffusion, the turquoise stick-like crystals of compounds $\{[ACrCu_2(C_2O_4)_4(bpy)_2]\cdot H_2O\}_n$ [A = K^+ (**1**) and NH_4^+ (**2**)] were grown from the reaction of an aqueous solution of $A_3[Cr(C_2O_4)_3]\cdot 3H_2O$ and methanol solution of $CuCl_2\cdot H_2O$ and 2,2'-bipyridine (bpy), in the molar ratio of 1 : 1 : 1. Structural analysis has showed that compounds **1** and **2** contain oxalate-bridged $[Cu(bpy)(\mu\text{-}C_2O_4)Cu(bpy)]^{2+}$ units mutually connected through oxalate groups from $[Cr(C_2O_4)_3]^{3-}$, forming ladder-like 1D chains (Figure 1a). Interestingly, in each of these complexes three different bridging modes of the oxalate ligand are observed. The change of *N*-donor aromatic ligand from bpy to 1,10-phenanthroline (phen) in the same reaction mixture influenced greatly the reaction outcome. Unusually, the $[Cr(C_2O_4)_3]^{3-}$ anions present in the starting solution have transformed to $Cr_2O_7^{2-}$, accompanied by oxidation of Cr^{III} to Cr^{VI} in an almost neutral solution. The obtained compound, yellow polyhedra of formula $\{[Cu_2(C_2O_4)(phen)_2(Cr_2O_7)]\}_n$ (**3**), contains ladder-like 1D chains, in which copper(II) ions from $[Cu(phen)(\mu\text{-}C_2O_4)Cu(phen)]^{2+}$ units are bridged through four oxygen atoms of $Cr_2O_7^{2-}$ anions (Figure 1b). This is the first known example of such extraordinary bridging mode of $Cr_2O_7^{2-}$. In addition to the single crystal X-ray diffraction study, characterization of the new complexes has been accomplished by means of the IR spectroscopy and thermal analysis.

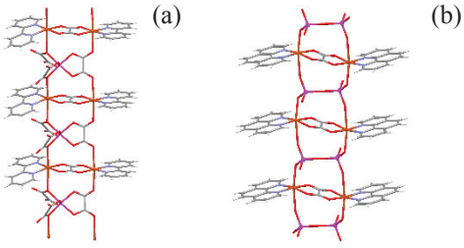


Figure 1: Ladder-like 1D chains made of (a) $[CrCu_2(C_2O_4)_4(bpy)_2]^-$ (**1** and **2**) and (b) $[Cu_2(C_2O_4)(phen)_2(Cr_2O_7)]$ (**3**).

THE PERSISTENCE OF DIMERIC $R^2_2(6)$ HYDROGEN BOND MOTIF IN CADMIUM(II) acac-BASED COMPLEXES

Postojanost dimernog motiva $R^2_2(6)$ u kadmijevim(II) kompleksima s derivatima acetilacetona

Boris-Marko Kukovec, Mladen Borovina, Marko Tomić, Marijana Đaković

Department of Chemistry, Faculty of Science, University of Zagreb, Zagreb, Croatia
E-mail: bkukovec@chem.pmf.hr

The self-assembly process with cobalt(II)/nickel(II) cations and dibenzoylmethanato (dbm)/hexafluoracetylacetonato (hfac) anions and multifunctional pyridine-oxime ligands (4-pyridinealdoxime, 4-Hoxpy; methyl 4-pyridyl ketoxime, 4-Meoxpy; 3-pyridinealdoxime, 3-Hoxpy; methyl 3-pyridyl ketoxime, 3-Meoxpy) was studied in order to target the desired supramolecular pattern - infinite 1D chains based on O–H···N(oxime) hydrogen bonds (dimeric $R^2_2(6)$ motif) [1]. The self-assembly process produced the desired 1D chains only in the case of $[Co(dbm)_2(3\text{-Meoxpy})_2]$, $[Ni(dbm)_2(3\text{-Meoxpy})_2]$ and all the hfac complexes prepared. The desired products were prepared by adjusting the reactants in an iterative manner to shift the magnitude of the electrostatic potential surfaces of competing hydrogen bond acceptor sites. Therefore, a robust synthetic protocol for the reproducible synthesis of the correct supramolecular products was obtained [1].

We further wanted to examine if the same trend of persistence of the dimeric $R^2_2(6)$ hydrogen bond motif could be observed in the analogous cadmium(II) acac-based complexes. Indeed, our preliminary results showed the presence of $R^2_2(6)$ motif in the crystal structure of $[Cd(hfac)_2(4\text{-Meoxpy})_2]$ (**1**) (Figure 1) and its absence in the crystal structure of $[Cd(dbm)_2(4\text{-Meoxpy})_2]$ (**2**) ($R^2_2(20)$ motif based on O–H···O(acac) hydrogen bonds was formed instead). In order to make the oxime N atom as good proton acceptor as possible and enable formation of the dimeric oxime motifs, it is not enough only to introduce an electron-donating methyl group in the vicinity of the oxime nitrogen atom, as it leads to the formation of $R^2_2(20)$ motif in **2**. The hydrogen-bond accepting power of the oxygen atom can be reduced by introducing electron-withdrawing substituents (fluorine atoms) at the acac-based ligand. This approach resulted with the desired $R^2_2(6)$ motif in **1**. The substitution of cobalt(II) or nickel(II) cations with larger cadmium(II) cation in the studied acac-based complexes results with the same general trend of $R^2_2(6)$ motif appearance, as established previously [1].

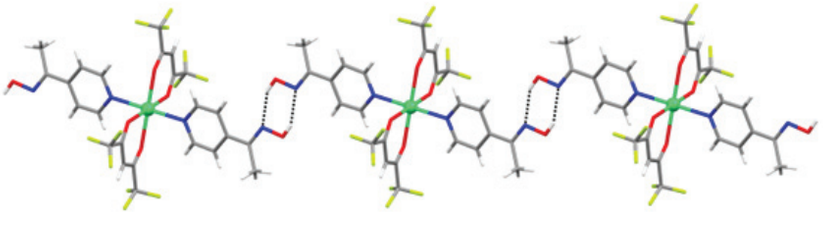


Figure 1: A dimeric $R^2_2(6)$ motif in the crystal structure of $[Cd(hfac)_2(4\text{-Meoxpy})_2]$ (**1**).

References

[1] B.M. Kukovec, M. Malik, I. Kodrin, C.B. Aakeröy and M. Đaković, *Cryst. Growth Des.* **16** (2016) 7308-7317.

Acknowledgements

This work has been fully supported by Croatian Science Foundation under the project UIP-11-2013-1809.

CRYSTALLIZATION AND STRUCTURAL STUDIES OF COBALT AND NICKEL BROMO-DERIVATIVES OF HUMAN INSULIN

Kristalizacija i strukturno istraživanje kobaltovog i niklovog bromo-derivata ljudskog inzulina

Biserka Prugovečki, Dubravka Matković-Čalogović

Laboratory of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10 000 Zagreb, Croatia
E-mail: biserka@chem.pmf.hr

Insulin is structured as two polypeptide chains, chain A consists of 21 and chain B of 30 amino acids. In the absence of metal ions native insulin crystallizes as a dimer but in the presence of zinc ions and some other cations three insulin dimers assemble into a hexamer. There are three forms of insulin hexamers: T_6, $T_3R_3^f$ and R_6 [1]. These forms of insulin are used in therapeutic preparations for the control of type 1 diabetes mellitus.

Due to its big medical importance structural data for more than two hundred human insulin derivatives can be found in the *Protein Data Bank* [2].

As a part of our ongoing research on the crystallization and structural studies on human insulin derivatives [3], in the present study cobalt and nickel were crystallized in high bromide concentration. Single crystals of the cobalt and nickel bromo-derivative of human insulin were grown by the hanging drop vapour diffusion method using Zn-free insulin (Figure 1). Diffraction data were collected at the ELETTRA Synchrotron, beam line XRD-1. The cobalt insulin derivative belongs to the trigonal crystal system while nickel derivative belongs to the tetragonal crystal system. Optimal crystallization conditions, coordination of cobalt and nickel ions in hexamer and conformation of the insulin molecule will be discussed.

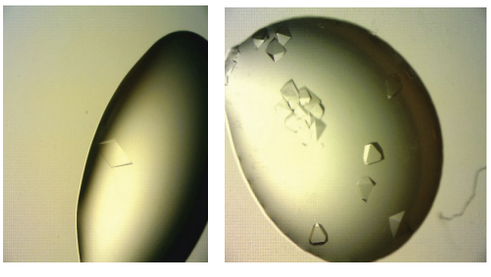


Figure 1: Single crystal of the human cobalt bromo-derivative of human insulin (left), single crystals of the nickel bromo-derivative of human insulin (right).

References

[1] N.C. Kaarsholm, H.C. Ko and M.F. Dunn, *Biochemistry* **28** (1989) 4427-4435.

[2] H.M. Berman, J. Westbrook, Z. Feng, G. Gilliland, T.N. Bhat, H. Weissig, I.N. Shindyalov and P.E. Bourne, *Nucleic Acids Res.* **28** (2000) 235-242.

[3] a) B. Prugovečki, E. J. Dodson, G. G. Dodson and D. Matković-Čalogović, *Croat. Chem. Acta*. **82** (2009) 433-438; b) B. Prugovečki, I. Pulić, M. Toth and D. Matković-Čalogović, *Croat. Chem. Acta*. **85** (2012) 435-439.

Acknowledgment

This work has been supported by the Foundation of the Croatian Academy of Sciences and Arts under the project Crystallization and structural studies of human insulin derivatives and protein HP1026 from *Helicobacter pylori*.

COBALT, NICKEL AND COPPER COMPLEXES WITH *N*-ALKYLGLYCINES: PREPARATION, STRUCTURAL, SPECTROSCOPIC AND THERMAL CHARACTERIZATION

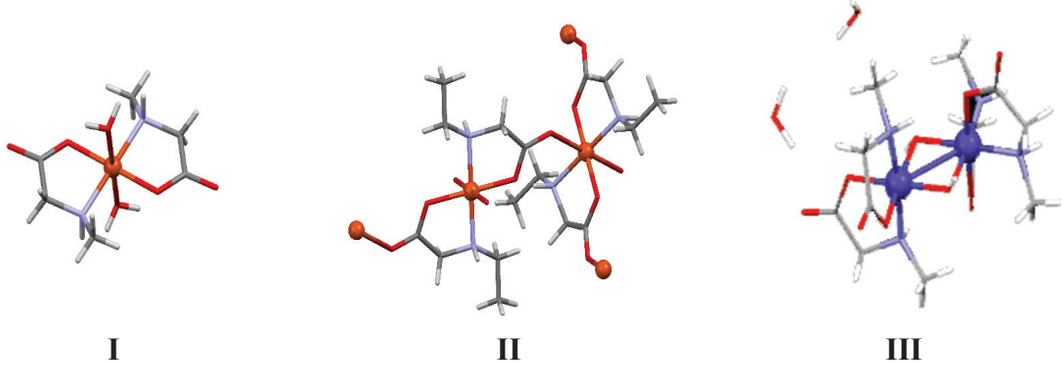
Kompleksi kobalta, nikla i bakra s *N*-alkilglicinima: priprava, strukturna, spektroskopska i termička karakterizacija

Neven Smrečki, Darko Vušak, Biserka Prugovečki, Dubravka Matković-Čalogović

Laboratory of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10000 Zagreb, Croatia
E-mail: nsmrecki@chem.pmf.hr

The most simple standard amino acid glycine, H_2NCH_2COOH (GlyH), is one of the most common chelating ligands [1]. Structural data for several hundred metal complexes with this ligand can be found in the *Cambridge Structural Database* [2], while complexes with N-methylglycine (sarcosine, CH_3NHCH_2COOH; SarH) appear to be quite rare. Metal complexes with higher N-alkylglycine derivatives were not known before this work. We have performed the reactions of copper(II), nickel(II) and cobalt(II) acetate with sarcosine and N-ethylglycine in aqueous solutions, and characterized the obtained complexes by X-ray crystallography, IR spectroscopy and thermoanalytical methods (TG/DTA and DSC).

Both amino acid derivatives in their anionic form act as N,O-bidentate ligands, forming three types of complexes. Complexes of the type **I** are monomeric species of the formula *trans*-$[M(Sar)_2(H_2O)_2]$ (M = Cu, Ni) or *trans*-$[M(Etgly)_2(H_2O)_2]$ (M = Co, Ni). Copper(II) complex with *N*-ethylglycine (type **II**) is a coordination polymer of the formula $[Cu(Etgly)_2]_n$ where the axial coordination sites are occupied by the carboxylate oxygen atoms from the neighbouring $[Cu(Etgly)_2]$ units. Cobalt(III) complex with sarcosine, $[Co(Sar)_2(\mu\text{-}OH)]_2 \cdot 2H_2O$ (type **III**), is a dimer containing the Co-Co bond. Details on the synthesis and structures of the complexes will be provided in the presentation.



I **II** **III**

Figure 1: Coordination environments around metal ions in the complexes $[Cu(Sar)_2(H_2O)_2]$ (**I**), $[Cu(Etgly)_2]_n$ (**II**) and $[Co(Sar)_2(\mu\text{-}OH)_2] \cdot 2H_2O$ (**III**).

References

[1] F.P. Dwyer and D.P. Mellor, *Chelating Agents and Metal Chelates*, Academic Press, New York, 1964.

[2] C.R. Groom, I.J. Bruno, M.P. Lightfoot and S.C. Ward, *Acta Cryst.* **B72** (2016) 171-179.

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF Cd(II) COORDINATION POLYMERS: SUPRAMOLECULAR ARCHITECTURES STABILIZED BY NONCOVALENT INTERACTIONS

Priprava i strukturna karakterizacija koordinacijskih polimera kadmija(II): Nekovalentnim interakcijama stabilizirane supramolekulske arhitekture

Željka Soldin, Nina Popov, Mladen Borovina, Marijana Đaković

Department of Chemistry, Faculty of Science, Horvatovac 102a, Zagreb, Croatia
E-mail: zeljka@chem.pmf.hr

Crystal engineering generally involves the design and synthesis of crystalline materials with desired properties and functions. Properties of crystalline solids are related not only to their composition but also to the manner in which building units are aligned and linked together in the solid state. Investigations of supramolecular interactions on metal-containing systems can therefore be divided into two pathways, (*i*) the study of assemblies primarily composed of 0D building units which are mutually linked *via* non-covalent interactions (in particular hydrogen and/or halogen bonds as the main crystal engineering tools), and (*ii*) the study of assemblies that rely on both coordination bond (1D- or 2D-coordination polymers) and much weaker and relatively reversible non-covalent interactions [1,2].

In order to investigate supramolecular assembles of solids composed of coordination polymers we synthesized a series of halide complexes of Cd(II) with halogen substituted pyridine and pyrimidine ligands. Single crystal X-ray structure determination revealed 1D-coordination polymers comprised of halide-bridged Cd(II) octahedra (Figure 1a). The building units are assembled into supramolecular 3D frameworks *via* a combination of hydrogen and halogen bonds (Figure 1b). Structure-property correlations, particularly thermal stability and elasticity, were investigated. Spectroscopic, thermal and structural data were accompanied by detailed data mining.

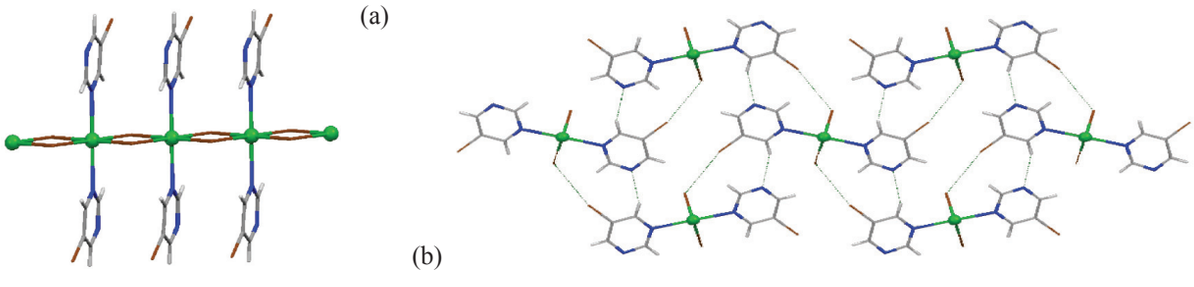


Figure 1: $CdBr_2(5\text{-Brpm})_2$ (5-Brpm = 5-bromopyrimidine): (a) 1D-coordination polymer; (b) supramolecular structure formed by C-H···N hydrogen bonds and Br···Br halogen bonds.

References

[1] L. Brammer, *Chem. Soc. Rev.* **33** (2004) 476-489.

[2] G. R. Desiraju, *J. Chem. Sci.* **122** (2010) 667-675.

Acknowledgments

This work has been fully supported by Croatian Science Foundation under the project UIP-11-2013-1809.

PREPARATION AND CHARACTERIZATION OF Zn(II) COMPLEXES WITH IMIDAZOLE AND 2-METHYLIMIDAZOLE

Priprava i karakterizacija kompleksa Zn(II) s imidazolom i 2-metilimidazolom

Marina Tašner, Andrea Gabud, Draginja Mrvoš-Sermek, Dubravka Matković-Čalogović

Departmant of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10000 Zagreb, Croatia
E-mail: mtasner@chem.pmf.hr

Complexes of imidazole and its derivatives with essential metal ions such as Zn(II), Cu(II) and Mn(II) have attracted much attention in recent years due to their antibacterial and antitumour properties [1]. They are also often used as structural models for certain metaloenzymes [2,3]. The biological role of complexes that contain an imidazole ring can be correlated with the two nitrogen atoms which have different properties; the deprotonated nitrogen atom can coordinate a transition metal atom, whereas the protonated nitrogen atom participates in hydrogen bonding [4].

Two novel zinc complexes with imidazole $[ZnX_2(Him)_2]$ (X = Cl, Br, Him = imidazole) were prepared by direct mixing of solid reactants without addition of liquid. Completion of the reaction was confirmed by powder X-ray diffraction. Single crystals were obtained by recrystallization from a methanol solution. Complex of zinc(II) with 2-methylimidazole, $[ZnCl_2(2\text{-Meim})_2]$, was prepared by heating the reaction mixture under reflux. In all of these complexes the Zn(II) atom is tetrahedrally coordinated by two nitrogen atoms from imidazole ligands and by two halide atoms. The complexes were characterized by IR spectroscopy, powder and single crystal X-ray diffraction methods.

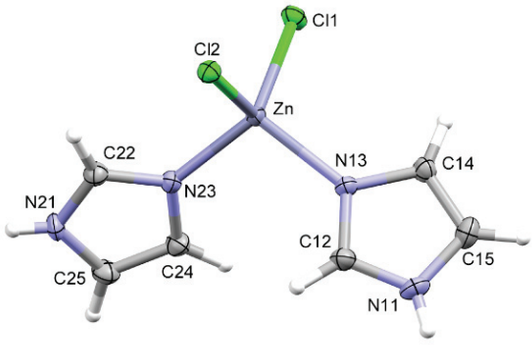


Figure 1: Molecular structure of $[ZnCl_2(C_3H_4N_2)_2]$.

References

[1] G. Zhoo and H. Lin, *Curr. Med. Chem.* **5** (2005) 137.

[2] S.P. Yang, Y.X. Tong, H.L. Zhu, H. Cao, X.M. Chen and L.N. Ji, *Polyhedron* **20** (2001) 223-229.

[3] A.A. Soayed, H.M. Refaat and D.A. Noor El-Din, *Inorg. Chim. Acta* **406** (2013) 230-240.

[4] Y. Gong, C. Hu, H. Li, W. Pan, X. Niu and Z. Pu, *J. Mol. Struct.* **740** (2005) 153-158.

STRUCTURAL STUDIES OF Zn(II) COMPLEXES OF (1,3-THIAZOL-2-YL)HYDRAZONES

Strukturna istraživanja Zn(II) kompleksa (1,3-tiazol-2-il)hidrazona

Aleksandar Višnjevac,[1] Jovana Araškov,[2] Nenad R. Filipović,[3] Tamara Todorović[2]

[1]*Institut Ruđer Bošković, Bijenička 54, Zagreb, Croatia*

[2]*Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, Belgrade, Serbia*

[3]*Faculty of Agriculture, University of Belgrade, Nemanjina 6, Belgrade, Serbia*

E-mail: aleksandar.visnjevac@irb.hr

Antimicrobial resistance is nowadays a serious public health threat. Therefore, there is an urgent need for development of new classes of antimicrobials [1]. Significant number of studies indicates promising antimicrobial activity of (1,3-thiazol-2-yl)hydrazones [2]. We recently reported structural and bioactivity studies on Co(III) complexes of 2-(2-(pyridine-2-ylmethylene)hydrazinyl)-4-(phenyl)-1,3-thiazole (HL^1), 2-(2-(pyridine-2-ylmethylene) hydrazinyl)-4-(4-metoxyphenyl)-1,3-thiazole (HL^2) and 2-(2-(pyridine-2-ylmethylene) hydrazinyl)-4-(4-tolyl)-1,3-thiazole (HL^3) [3].

Here we present the structural studies of a series of their zinc complexes, prepared by simple reactions of $ZnCl_2$ and $Zn(NO_3)_2$ with $HL^{1–3}$: $[ZnCl_2(HL^1)]$ (**1**), $[Zn(HL^1)_2](NO_3)_2 \times H_2O$ (**2**), $[Zn(HL^2)_2][ZnCl_4]$ (**3**), $[Zn(HL^2)_2](NO_3)_2 \times MeOH \times H_2O$ (**4**), $[Zn(HL^3)_2][ZnCl_4]$ (**5**) and $[Zn(HL^3)_2](NO_3)_2 \times 3H_2O$ (**6**). Complexes were characterized by elemental analysis, molar conductivity measurements, UV-Vis, IR and NMR spectroscopic analyses. Single crystal X-ray analyses of **1**–**5** were accomplished. Structure of **1** is characterized by 1:1, while all other complexes reveal 1:2 metal to ligand ratio. In all complexes, the tridentate *NNN* coordination is observed. In **1** zinc is located in a centre of a distorted trigonal bipyramid. In cationic complexes of **2**, **3**, **4** and **5**, distorted octahedral coordination cores are observed and the overall charge is balanced by the presence of two nitrate anions (**2** and **4**) or two $ZnCl_4^{2-}$ anions (**3** and **5**). Crystal structure of **1** is characterized by the H-bonded centrosymmetric dimers of a graph-set notation $R(2,2)10$. In **2** and **4**, two hydrazine nitrogen atoms act as donors in a bifurcated H-bonds, connecting ligand molecules to O atoms from the corresponding nitrates. H-bonding patterns in **3** and **5** are analogous. A single observed H-bond connects the hydrazine nitrogen to a chlorine from the $ZnCl_4^{2-}$ anion as an acceptor, hence an "endless" chain is formed parallel to the crystallographic *a* axis.

References

[1] A. Borges, C. Ferreira, M.J. Saavedra and M. Simões, *Microb. Drug Resist.* **19** (2013) 256-265.

[2] H. Elshaflu, S. Bjelogrlić, C.D. Muller, T.R. Todorović, M. Rodić, A. Marinković and N.R. Filipović, *Coord. Chem.* **69** (2016) 3354-3366.

[3] N.R. Filipović, H. Elshaflu, S. Grubišić, Lj.S. Jovanović, M.V. Rodić, I. Novaković, A. Malešević, I. Djordjević, H. Li, N. Šojić, A. Marinković and T.R. Todorović, *Dalton Trans.* (2017) DOI: 10.1039/C6DT04785H

INTERNATIONAL YEAR OF CRYSTALLOGRAPHY, IYCr2014, IN CROATIA

Croatian Crystallographic Association, CCA
Croatian Association of Crystallographers, CAC

1) Scientific Meeting *Contemporary Crystallography in Croatia*, dealing with the present studies and perspectives, Zagreb, September 30, 2014, organized by the Croatian Crystallographic Association, under the auspices of the Croatian Academy of Sciences and Arts; the Chair of the Organizing Committee Stanko Popović (spopovic@phy.hr).

2) *Proceedings* of the Scientific Meeting *Contemporary Crystallography in Croatia* (25 papers), published by the Croatian Academy of Sciences and Arts, Zagreb, in 2015, in Croatian with extended abstracts in English; Editor of the *Proceedings* Stanko Popović (spopovic@phy.hr).

3) *Hot Topics in Contemporary Crystallography*, Workshop for young crystallographers; lecturers: eminent European crystallographers; organized by the Croatian Association of Crystallographers, Chair of the Organizing Committee Aleksandar Višnjevac (aleksandar.visnjevac@irb.hr), May 10th to 15th, 2014, Šibenik, Croatia.

4) *23rd Slovenian-Croatian Crystallographic Meeting*, June 18–22, 2014, Slovenia, devoted to *IYCr2014*, organized by the Slovenian Crystallographic Society (Anton Meden, Anton.Meden@uni-lj.si) and the Croatian Crystallographic Association (Stanko Popović, spopovic@phy.hr); the Book of Abstracts (in English) published by the Slovenian Crystallographic Society; promotion of ECM29.

5) *Website* of the Croatian Crystallographic Association (**www.hazu.hr/kristalografi**) and of the Croatian Association of Crystallographers (www.hrvatska-udruga-kristalografa.hr) containing news on *IYCr2014*; web masters Aleksandar Višnjevac, Ana Šantić.

6) *Popular lectures on Crystallography* in professional societies in Croatia: Croatian Chemical/ Physical/ Biological/ Geological/ Pharmaceutical ... Society, presented by members of the CCA and the CAC; one of the sources of information: the Promotion brochure *Crystallography matters*!, edited by IUCr and UNESCO, translated in Croatian.

7) *Popular lectures on Crystallography* in secondary schools, presented by members of the CCA and the CAC; one of the sources of information: the Promotion brochure *Crystallography matters*!, edited by IUCr and UNESCO, translated in Croatian.

8) *English-Croatian Dictionary of Crystallography, Physics of Condensed Matter and Materials Science,* containing 1710 terms with a short description of each term; authors Stanko Popović (spopovic@phy.hr), Antun Tonejc (atonejc@phy.hr) and Milica Mihaljević (mmihalj@ihjj.hr); published in 2014 by the Institute of the Croatian Language and Linguistics.

9) *Hundred years of Crystallography*, a review, in Croatian journal *Chemistry in Industry* **62** (2013) 247-260; authors Biserka Kojić Prodić (kojic@irb.hr) and Krešimir Molčanov (kmolcano@irb.hr).

10) *Chemical Crystallography before X-ray Diffraction*, a review in *Angewandte Chemie Int. Ed.* **53** (2014) 638–652; authors Krešimir Molčanov (kmolcano@irb.hr) and Vladimir Stilinović (vstilinovic@chem.pmf.hr).

11) *IYCr2014 – one hundred years of exploring the world of atoms*, a lecture presented by Stanko Popović (spopovic@phy.hr) before the Croatian Academy of Sciences and Arts, Zagreb; November 20, 2013; April 24, 2014.

12) *Nikola Tesla, scientist and inventor, and the discovery of X-rays*, a lecture presented by Stanko Popović (spopovic@phy.hr) at the Meeting *The Scientific and Technological Legacy of Nikola Tesla*, organized by the Croatian Academy of Sciences and Arts, Zagreb, December 17, 2013; also presented before the Croatian Academy of Sciences and Arts, Zagreb, November 11, 2014.

13) *Postgraduate courses on contemporary crystallography*, held by Senior scientists and University professors, members of the CCA and the CAC.

14) *Popular Crystallography*: TV, radio, newspaper, presented by members of the CCA and the CAC.

15) *Crystal-growing competition*, organized by Ernest Meštrović (ernest.mestrovic@pliva.com), Pliva, CCA and CAC; participants in competition pupils in secondary schools, the best works rewarded, the valuable results of competition will be used for the moving exhibition throughout Croatia (museums, institutions, companies), the useful material will be collected for promotion of crystallography in Croatia.

16) The Promotion brochure *Crystallography matters*!, edited by IUCr and UNESCO, translated in Croatian and published in the Croatian journal *Chemistry in Industry* 63 (2014) 217-225.

17) A special issue of the Croatian journal *Priroda* (*Nature*), No. 6, 2014, devoted to IYCr2014, containing 12 papers on crystallography written by Croatian crystallographers, members of the CCA and the CAC; editors Nenad Judaš, Vladimir Stilinović.

Znanstveno vijeće za kristalografiju HAZU
Hrvatska kristalografska zajednica

Nakladnik
HRVATSKA AKADEMIJA ZNANOSTI I UMJETNOSTI
Trg Nikole Šubića Zrinskog 11, 10000 Zagreb

Za nakladnika
Akademik Pavao Rudan, glavni tajnik

Grafički urednik
Ranko Muhek

Naklada
300 primjeraka

Tisak
Stega tisak d.o.o.

Zagreb, kolovoz 2017.

ISBN 978-953-347-169-3

ISBN 978-953-347-169-3

Cljena: 70,00 kn