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SERBIAN CRYSTALLOGRAPHIC SOCIETY

XIX КОНФЕРЕНЦИЈА СРПСКОГ КРИСТАЛОГРАФСКОГ ДРУШТВА

Изводи радова

XIX CONFERENCE OF THE SERBIAN CRYSTALLOGRAPHIC SOCIETY

Abstracts

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PLENARY LECTURES

ПЛЕНАРНА ПРЕДАВАЊА

UNUSUAL PROPERTIES OF Mn(III) COMPLEXES RELATED WITH LATTICE EFFECTS

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A series of isostructural, isomorphic Mn(III) complexes based on 5MeO-salen (5,5-Methoxy bis (salicylidene-imine) and acetate ligands, namely $[Mn_2(5MeOsalen)_2(RCOO)]X$, $R=CH_3$; $X=ClO_4^-$ (**1**), PF_6^- (**2**), $CF_3SO_3^-$ (**3**), shows different magnetic properties as function of detailed packing factors determined by the counter anion X. The systems are based on $\{Mn_2\}$ dimeric units with intrinsic ferromagnetic behavior, but their overall manifestation is an antiferomagnetic one, determined by the coupling along the carboxylate bridges. Another variety based on similar units $[Mn_2(naften)_2(RCOO)(R'OH)]X$, $R=CH_3$; $R'= CH_3$ (**4**), C_2H_5 (**5**), $X = PF_6^-$ shows unusual short hydrogen bonds in a homo-metalic Mn(III) chain with overall ferromagnetic coupling. In this case the ferromagnetic behavior is predominant because of the limited interaction between the dimeric units. Aside the interaction along the bridges there is a long range interaction between the aromatic groups of salen and naften group ligands.

Another manifestation of crystal packing was found in the case of a family of mononuclear Mn(III) complexes with derivatives of a hexadentate Schiff base ligand, $[Mn^{III}(X\text{-sal-}N(1,5,8,12))]ClO_4$. The strong field nature of the ligand brings the coordination bonding regime near to the crossing between HS and LS states. The marginal substituents, X, decide via packing effects the final properties in the solid state. Thus for X=3MeO the system is HS, while for the X=napfth is LS and for X= 4Br, 5MeO, exhibit spin crossover at 150 K and 250 K, respectively. The LS and spin crossover systems are rare situation in the Mn(III) chemistry. The dynamics and the cooperativity effects of the lattice exert a crucial role in the spin crossover event, proving the subtle balance between molecular and supramolecular effects.

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NPLIN : A NEW EXPERIMENTAL DEVICE FOR LASER INDUCED NUCLEATION

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The study of polymorphism of pharmaceutical compounds is a growing field of activity. This is due, on one hand, to the economic pressure of the pharmaceutical industry, and on the other hand, to the more important awareness of the polymorphism (or pseudo-polymorphism) consequences on the properties of a medication (chemical and physical stability, solubility, dissolution rate, bioavailability, mechanical properties, manufacturing process…).Ideally, the experimental study of polymorphism necessitates the mastery of crystallization of desired polymorphic forms and the obtainment of not-yet-characterized phases. An original method of nucleation, "Non Photochemical Light Induced Nucleation" (NPLIN), makes possible nucleation control on the nanoscale by using the polarization properties of a pulsed laser (pulse length about 10 nanoseconds).

We propose to demonstrate the feasibility and the potential of this method applied to an "Active Pharmaceutical Ingredient" (API), and to apply this method on active molecules with a real issue in the context of polymorphism in order to bring answer elements to the specific problem posed. The three target APIs we would like to study are: a)Compounds displaying problems of crystallization or having not-yet-resolved polymorphism, b) Chiral compounds for which the use of the NPLIN method could permit a crystallization of the two enantiomers from a racemic mixture and c)Compounds frequently used in the framework of active pharmaceuticals, called model compounds.

In order to demonstrate the feasibility and the potential of this method applied to APIs, we will formulate and perform nucleation experiments by controlling all parameters not only during the solution preparations (humidity control, atmosphere, …) but also at the optical level (power control, wavelength, polarization, …). We will also work on the development and performance of experimental set-ups combined with X-ray diffraction in order to follow *in situ* the kinetics of crystallization and to better understand the nucleation phenomenon. These experimental studies will be complemented by the development of new tools for modeling the involved mechanism in the nucleation process and the interaction with the nanosecond pulse of a polarized laser light; the idea behind this is to describe these nano-objects (few tens of molecules) by using *ab initio* methods for the core and dynamic methods for the surface of the particles.

Experimental results, modeling, and statistical studies of the crystal packing of the target compounds will be combined in order to conclude about the NPLIN method action at the nanoscale and to predict which API could be a good candidate for this method of crystallization. In parallel, we will try to give answer to the APIs considered problematic by studying: a)Thermodynamic aspects of the relative stability of the different compounds and b)Electronic and electrostatic properties of the target compounds through a fundamental approach combining both high resolution X-ray diffraction and *ab initio* theoretical

calculations. With this approach, we will be able to get a better understanding of phenomena linked to solubility and bioavailability requiring knowledge of molecular interactions in the crystal; in other words, we will try to understand the polymorphism of the active molecules and the impact on their physiochemical properties. The expected results can be summarized as follows: a) To get a better understanding of nucleation mechanisms under an intense electric field at the nanoscale in order to master this new crystallization technique and b) To provide a better understanding of the problematic polymorphisms of about ten selected active molecules. Finally, these studies can lead, in pharmaceutical manufacturing, to a new control technique in the production of a specific polymorph phase of an active molecule.

NPLIN: NOVI EKSPERIMENTALNI PRISTUP ZA LASEROM INDUKOVANU NUKLEACIJU

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Ispitivanje polimorfizma farmaceutskih jedinjenja je rastuće polje istraživanja. Ovo je posledica, s jedne strane, ekonomskog pritiska farmaceutske industrije, a sa druge strane, rastućeg značaja posledica polimorfizma (ili pseudo-polimorfizam) na osobine leka (hemijska i fizička stabilnost, rastvorljivost, stopa disolviranja, bioraspoloživost, mehaničke osobine, proces proizvodnje ...). Idealno, eksperimentalna studija polimorfizma iziskuje savladavanje kristalizacije željenih polimorfnih oblika i dobijanje još nekarakterisanih faza. Originalni metod nukleacije, "Ne Fotohemijski Svetlosno Indukovana nukleacija" (NPLIN), omogućava kontrolu nukleacije na nano nivou pomoću pulsnog lasera (dužina oko 10 nanosekundi) sa polarizacionim osobinama.

Mi predlažemo demonstraciju izvodljivosti i mogućnosti ovog metoda primenom na "aktivne farmaceutske sastojke (API)" i primenu na aktivne molekule sa pravim pitanjem u kontekstu polimorfizma kako bi se dobio odgovor na konkretan problem. Tri ciljne API koje želimo da izučavamo su: a) Jedinjenja koja pokazuju probleme kristalizacije ili koja imaju još nerešen polimorfizam, b) Hiralna jedinjenja za koje upotreba NPLIN metoda može dozvoliti kristalizaciju enantiomera iz recemske smeše, c) Jedinjenja koja se često koriste u okviru aktivnih farmaceutika i koja se nazivaju model jedinjenja. Sa ciljem da se pokaže izvodljivost i mogućnost primene ovog metoda na API, mi ćemo osmisliti i realizovati eksperimente nukleacije kontrolišući sve parametre, ne samo tokom priprema rastvora (kontrola vlažnosti, atmosfera, ...), već i na optičkom nivou (kontrola snage, talasna dužina, polarizacija, ...). Takođe ćemo raditi na koncepciji i realizaciji eksperimentalnih uslova kombinovanih sa difrakcijom rendgenskog zračenja u cilju praćenja „in situ" kinetike kristalizacije i boljeg razumevanja fenomena nukleacije. Ova eksperimentalna istraživanja će biti komplementirana razvojem novih alata za modelovanje posmatranih mehanizama u procesu nukleacije i interakcije sa nanosekundskim pulsom polarizovane laserske svetlosti; ideja je da se opišu ovi nano-objekti (nekoliko desetina molekula) pomoću *ab initio* metode za osnovne i dinamičke metode za površine čestice.

Eksperimentalni rezultati, modelovanje i statističke studije kristalnog pakovanja ciljnih jedinjenja će biti kombinovane kako bi se doneli zaključci o delovanju NPLIN metoda na nano nivou i da se predvide koji API mogu biti dobri kandidati za ovu metodu kristalizacije.

Paralelno s tim, mi ćemo pokušati da damo odgovor na ovo izučavanje AMI-ja proučavajući: a) Termodinamičke aspekte relativne stabilnosti različitih jedinjenja i b) Elektronske i elektrostatičke osobine ciljnih jedinjenja kroz fundamentalne pristupe kombinujući eksprimente difrakcije rendgenskog zračenje visoke rezolucije i *ab initio* teorijska izračunavanja. Sa ovim pristupom, mi ćemo moći da bolje razumemo fenomene

vezane za rastvorljivost i bioraspoloživost, koji zahtevaju poznavanje molekulskih interakcija u kristalu; drugim rečima, pokušaćemo da razumemo polimorfizam aktivnih molekula i uticaj na njihove fizičko-hemijske osobine. Očekivani rezultati se mogu rezimirati na sledeći način: a) Bolje razumevanje mehanizma nukleacije pod intenzivnim električnim poljem na nano nivou kako bi se savladala ova nova tehniku kristalizacije i b) Bolje razumevanje problematike polimorfizma desetak odabranih aktivnih molekula.
Konačno, ove studije u proizvodnji lekova mogu dovesti do nove tehnike kontrole u proizvodnji određene polimorfne faze aktivnog molekula.

SYNTHESIS AND CHARACTERIZATION OF COMPLEXES OF SOME TRANSITION METALS WITH ETHYLENEDIAMINE-*N,N'*-DI-*S,S*-2-PROPANOIC ACID

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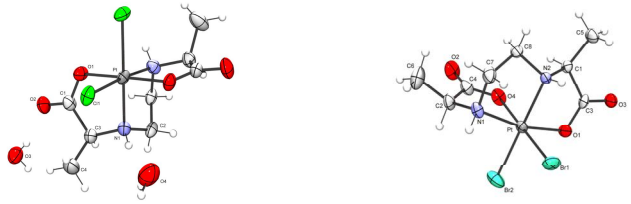
The tetradentate ligand ethylenediamine-*N,N'*-di-*S,S*-2-propanoic acid was obtained by direct reaction of sodium salt of *S*-alanine and 1,2-dibromethane. The structure of the isolated ligand was determined by infrared, ^{1}H and ^{13}C NMR spectroscopy, as well as by X-ray analysis [1]. Ethylenediamine-*N,N'*-di-*S,S*-2-propanoic acid was unexpectedly crystallized in form of monohydrochloride.

The ligand was used for the synthesis of the corresponding complexes of chromium(III) [2], ruthenium(III) [3] and platinum(IV) [4]. The composition of the prepared octahedral complexes was confirmed by elemental microanalysis, and the structure was determined on the basis of infrared, electronic absorption, circular-dichroism spectra, nuclear magnetic resonance spectroscopy (^{1}H and ^{13}C NMR) and by X-ray analysis. In medicinal chemistry, metal complexes have gained considerable attention as pharmaceuticals being used as chemotherapeutic drugs mainly against cancer. Despite the large amount of compounds synthesized and tested only a small number have advanced to the late stages of clinical development. In order to overcome the severe side-effects of a platinum-based chemotherapy, to improve clinical effectiveness and to broaden the spectrum of activity there is still a need for novel platinum antitumor agents.

Compared to cisplatin as a referent platinum-based anticancer drug, novel platinum(IV) compounds [$PtCl_2$(*S,S*-eddp)] and [$PtBr_2$(*S,S*-eddp)] displayed significantly lower cytotoxic activity towards L929 fibrosarcoma and C6/U251 glioma cell lines.



[1] V. V. Glođović, G. P. Radić, S. M. Stanić, F. W. Heinemann and S. R. Trifunović, *J. Serb. Chem. Soc.* **76 (7)** (2011) 995-1001.
[2] V. V. Glođović, F. W. Heinemann and S. R.Trifunović, *J. Chem. Crystall.* **38** (2008) 883-889.
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SINTEZA I KARAKTERISANJE KOMPLEKSA NEKIH PRELAZNIH METALA SA ETILENDIAMIN-*N,N'*-DI--*S,S*-2-PROPANSKOM KISELINOM

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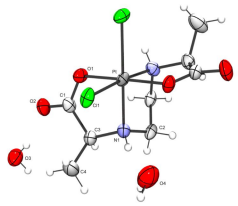
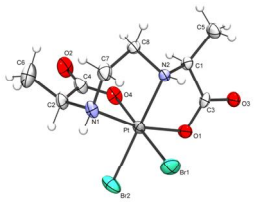
Tetradentatni ligand, etilendiamin-*N,N'*-di-*S,S*-2-propanska kiselina, je dobijen direktnom reakcijom natrijumove soli *S*-alanina i 1,2-dibrometana. Struktura izolovanog liganda utvrđena je na osnovu infracrvene, ^{1}H i ^{13}C NMR spektroskopije, kao i na osnovu rendgenske strukturne analize [1]. Etilendiamin-*N,N'*-di-*S,S*-2-propanska kiselina je neočekivano kristalisala u obliku monohlorhidrata.

Dobijeni ligand je korišćen za sintezu odgovarajućih kompleksa hroma(III) [2], rutenijuma(III) [3] i platine(IV) [4]. Sastav nagrađenih oktaedarskih kompleksa potvrđen je elementalnom mikroanalizom, dok je struktura utvrđena na osnovu infracrvenih, elektronskih apsorpcionih, cirkularno-dihroičnih spektara, nuklearno-magnetne razonancione spektroskopije (^{1}H i ^{13}C NMR) i na osnovu rendgenske strukturne analize.U medicinskoj hemiji, kompleksi metala su privukli značajnu pažnju kao farmaceutski agensi korišćenjem u hemioterapiji, posebno protiv tumora. Uprkos velikom broju sintetisanih i testiranih jedinjenja samo je mali broj njih ušao u dalja klinička ispitivanja. U cilju prevazilaženja negativnih sporednih efekata hemioterapije, pobaljšanju klinične efikasnosti i proširivanju spekta aktivnosti neophodno je sintetisani nove platinske antitumorske agense.

Poređenjem sa cisplatinom, kao referetnim antikancerogenim lekom, dva novosintetisana kompleksa [$PtCl_2$(*S,S*-eddp)] i [$PtBr_2$(*S,S*-eddp)], su pokazala značajno manju citotoksičnu aktivnost prema L929 fibrosarkomu i C6/U251 ćelijskim linijama glioma.





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NON-COVALENT INTERACTIONS IN TRANSITION METAL CHEMISTRY: FROM MOLECULAR COHESION TO MOLECULAR DESIGN

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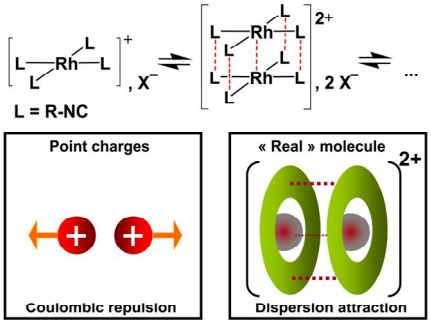

Keywords: coordination chemistry, organometallics, DFT-D, catalysis and molecular design.

Non-covalent interactions[1] are ubiquitous in Nature[2] and their accurate description remains a difficult task.[3] Nonetheless, *van der Waals* interactions, which constitute rather conventional classes of interactions, have been shown to contribute greatly to the stereo-specificity of chemical processes in natural systems. Because of their directionality in most cases and in spite of the relative unpredictability of their effectiveness, these interactions are increasingly being called upon and considered for the rational synthetic design[4] of supramolecular assemblies[5] and coordination polymers[6] and in nanomolecular construction.[7] Understanding them and being able to analyze the origins of those interactions remains a challenge to both the theoreticians and the experimentalists.
Our recent studies[8] have provided indication on the involvement of dispersion forces (London forces) in 3d transition metal complexes containing weak intra-molecular inter-metallic interactions. These aspects will be emphasized with critical examples that suggest among other things that the *d-d* interaction paradigm requires revision. We will also show through our most recent findings that the design of apparently challenging systems can be based on the rational analysis and use of non-covalent interactions.

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"FORGET THE CRYSTALS: WE ALREADY HAVE A COMPUTER": A CRITICAL DISCUSSION OF SOME RECENT COMPUTATIONAL PREDICTIONS ON BIOLOGICALLY-RELEVANT SYSTEMS

Radu Silaghi-Dumitrescu

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Computational chemistry offers itself as a non-invasive approach for studying chemical and biochemical structures and phenomena. The increasing availability of large-scale computing resources allows computational chemists to perform 'thought experiments' (simulations) spanning a range of observables far greater than available to wet chemistry experiments (although we usually refer to computational/theoretical experiments as 'theory', and wet chemistry experiments as 'experiments', the border between the two categories is, and should be, fading). Theoretical methods have been or are being developed to predict all experimentally-measured properties, including structure, reactivity, spectroscopy, and biological action. Here, we discuss our recent findings on modeling proteins with ab initio and DFT techniques, with emphasis on secondary structure predictions. We illustrate the degree to which correlations can be made with experimentally-known preferences (including the Ramachandran plots), and the perhaps unexpected limitations thereof - in the context of systems based on non-covalent interactions. We also discuss results obtained from modeling the interaction of small molecules with metal centers based on transition metals (with such topics as nitric oxide, nitrite, molecular oxygen, and heme-type systems, iron-sulfur sites, or copper sites) pointing out not only the strong points of the DFT methods but also their intrinsic limitations in predicting metal-ligand interactions.

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CRYSTALLOGRAPHY – QUO VADIS?

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In this talk I shall share some personal thoughts concerning current situation and future development of crystallography. Ideas will be arranged about own recent diffraction experiments along with ongoing developments of instrumentation in the home laboratory. Topics will include improved data quality, size confinement, real structure as well as additional information from complimentary and independent methods. Particular emphasis will be on the discussion of certain borderlines, i.e. powder diffraction vs. single crystal diffraction or absorption contrast vs. phase contrast. Are these borders going to disappear or does this even create new science? How are we going to teach in the years to come? Obviously, I am hoping for critical feedback and vital discussions.

EXTREME DISORDER EFFECTS IN $M(TCNE)_2$ MATERIALS ($M=V^{II}, Mn^{II}, Fe^{II}$, $TCNE^-$ = TETRACYANOETHYLENE)

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The serendipitous discovery of $V(TCNE)_x$ (x~2) as a molecular magnet with room critical temperature[1] attracted the interest on TCNE systems, recent discoveries revealing applications in spin valves[2] and spin-polarized transport in light-emitting diodes.[3] However the full advance in understanding the key factors of magnetic and spin dynamic properties have been hindered by persisting failures in determining crystal structure of such systems, the situation causing uncertainity and controversies.[4,5] Starting from the limited structural information, pointing a a quasi-octahedral coordination of the metal center,[6] with almost homogeneous bond lengths, all about 2 Å, using chemical intuition and state of the art computational methods, we advanced a consistent model of the $M(TCNE)_2$ ideal crystal lattice. This structure is prone to static and dynamic disorder effects, explaining in this way the lack of a proper crystallographic characterization. The proposed crystal geometry is optimized using Density Functional Theory (DFT) calculations with periodic boundary conditions. The DFT calculations indicate antiparallel spin alignment resulting in ferrimagnetic ordering. A key issue of our modeling is the explanation offered for the propensity of the proposed crystal structure to undergo disorder and defects, which correlates well with the random anisotropy behavior, observed experimentally.

Acknowledgement: This work is supported by the Romanian Ministry of Education and Research through the CNCS-UEFISCDI research grant PN2-Idei-PCCE-239/2010, contract no. 9/2010.

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INVESTIGATION ON VANADATE FLUX GROWN SINGLE CRYSTALS IN $K_{1-x}(Na,Li)_xAlSiO_4$ SYSTEM

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The single crystals were obtained applying vanadate flux growth technique with various starting nominal compositions ($KAlSiO_4$; $K_{1-x}Na_xAlSiO_4$; $K_{1-x}Li_xAlSiO_4$; $x < 0.3$). X-ray diffraction experiments revealed three groups of the structures: a) $KAlSiO_4$ – *O1*, monoclinic structure [1]; b) hexagonal kalsilite-like phases with tridymite framework topology that incorporate Li and Na in the K-sites, similar to [2]; and c) Na-rich tetragonal leucite structures with space group symmetry lower than $I\,4_1/a$ [3].

First two groups of the crystals exhibit various degree of diffuse scattering effects (Fig. 1). Furthermore, almost all the crystals are affected by multiple twinning. Chemical compositions deduced from the refinements show good agreement with SEM EDS investigations.

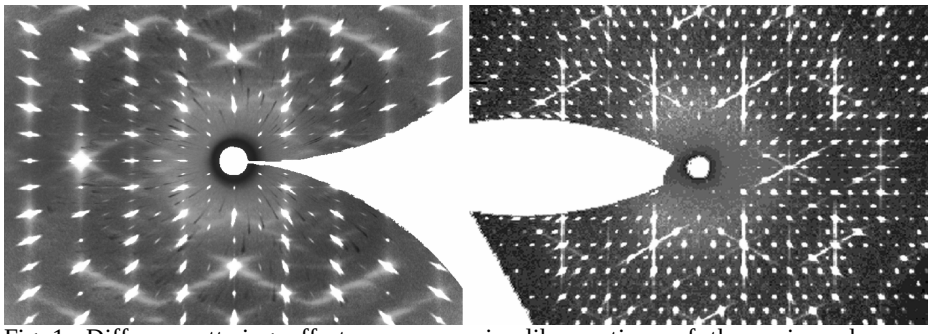

Fig 1. Diffuse scattering effects on precession-like sections of the reciprocal space reconstructed from X-ray diffraction experiments in $K_{0.7}Na_{0.3}AlSiO_4$ (left) and $KAlSiO_4$ – *O1* (right).

Financial support by the Swiss National Science Foundation (SNSF) through the grant IZ73Z0-127961 is gratefully acknowledged.

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ISPITIVANJE MONOKRISTALA IZ SISTEMA $K_{1-x}(Na,Li)_xAlSiO_4$ DOBIJENIH KRISTALIZACIJOM IZ VANADATNOG FLUKSA

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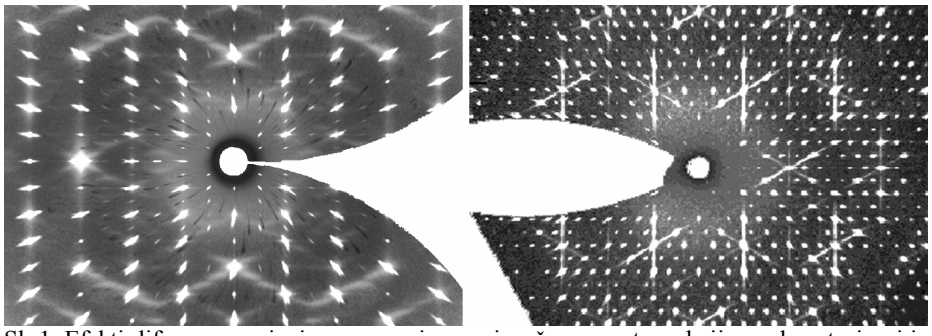
Monokristali su dobijeni kristalizacijom iz vanadatnog fluksa sa različitim polaznim nominalnim sastavom nutrijenta ($KAlSiO_4$; $K_{1-x}Na_xAlSiO_4$; $K_{1-x}Li_xAlSiO_4$; $x < 0,3$). Rezultat ispitivanja difrakcijom rendgenskog zračenja su tri grupe struktura: a) $KAlSiO_4$ – *O1* monoklinična struktura [1]; b) heksagonalne kalsilitske faze sa tridimitskom mrežnom topologijom slične [2], koje sadrže Li i Na u K-položajima; i c) tetragonalni leuciti bogati natrijumom sa simetrijom nižom od prostorne grupe $I\,4_1/a$ [3].

Rendgenska difrakcija prve dve grupe kristala pokazuje različit stepen difuznog rasejanja (sl. 1), dok su gotovo svi ispitivani kristali višestruko bližnjeni. Hemijski sastavi dobijeni utačnjavanjem se dobro slažu sa hemijskim sastavima izračunatim iz SEM EDS ispitivanja.



Sl. 1. Efekti difuznog rasejanja na presecima recipročnog prostora, koji su rekonstruisani iz rezultata rendgenske difrakcije na monokristalu kod: $K_{0.7}Na_{0.3}AlSiO_4$ (levo) i $KAlSiO_4$ – *O1* faze (desno).

Ovo istraživanje finansijski je pomogao Švajcarski nacionalni naučni fond (SNSF), ugovor IZ73Z0-127961.

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ORAL PRESENTATIONS

САОПШТЕЊА

X-RAY STRUCTURE DETERMINATION OF THE PROTEIN COMPLEX EPSILON-ZETA(234stop)

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Structure determination of proteins with almost equal sequences can be accomplished with the molecular replacement (MR) method. This method is valuable especially when variants of previously crystallized proteins are being studied. Here we present the crystal structure of the ez(234stop) antitoxin-toxin complex with the z toxin shortened from 284 to 233 amino acids from the C-terminal. We have shown that the C-terminal domain, consisting of a helix-turn-helix motif, although not a part of its ATP binding pocket, is crucial for the zeta protein toxicity in *E. coli*. We have constructed this non toxic variant of the zeta toxin and successfully expressed it without the cognate antitoxin e in the *E. coli* expression host. Crystallization of the toxin was only successful in a heterotetrameric complex with the antitoxin e. The low-copy number broad-host range plasmid pSM19035 [1], on which this antitoxin-toxin system is encoded, has two distinctive regions responsible for its maintenance. The second, segB region, encodes genes for four proteins, among them proteins e and z which form the antitoxin-toxin complex where e represents the proteic antitoxin and z the proteic toxin. In plasmid free daughter cells the delicate balance between the stability of the toxin z and its antitoxin e is disrupted in favor of the toxin, which leads to cell filamentation of plasmid free daughter cells and, consequently, to cell death.

The structure of this protein complex was determined by molecular replacement (MR) technique using the structure of the full- length proteins [2] ez as the search model. Native data were collected with a resolution of 2.50 Å, data reduction and scaling was performed with Denzo and Scalepack, molecular replacement with PHASER and structure refinement with CNS.

[1] Alonso, J. C., Balsa, D., Cherny, I., Christensen, S. K., Francuski, D., Gazit, E., et al. (2007). Bacterial Toxin-Antitoxin Systems as Targets for the Development of Novel Antibiotics. In R. A. Bonomo, & M. E. Tolmasky (Eds.), *Enzyme-Mediated Resistance to Antibiotics: Mechanism, Dissemination, and Prospects for inhibition* (pp. 313-329). Washington, D.C.: ASM Press.

[2] Meinhart, A., Alonso, J. C., Sträter, N. and Saenger, W. (2003). Crystal Structure of the Plasmid Maintenance System e/z: Functional Mechanism of Toxin z and Inactivation by e_2z_2 Complex Formation. Proc. Natl. Acad. Sci. (US) **100:** 1661-1666.

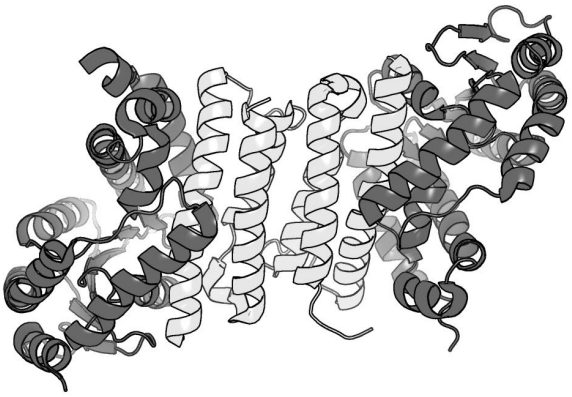

Figure 1. The heterotetrameric antitoxin e (light gray) and toxin z (black) complex

RENDGENSKA STRUKTURNA ANALIZA PROTEINSKOG KOMPLEKSA EPSILON-ZETA(234stop)

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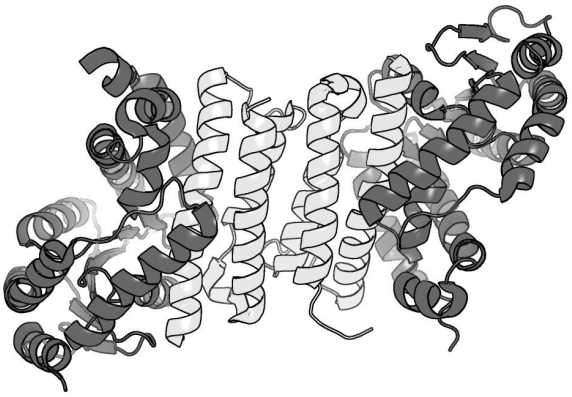
Određivanje trodimenzionalnih struktura makromolekula pomoću metode molekularne zamene (MR) je dragocena metoda naročito u slučajevima kada se radi određivanje struktura varijanti makromolekula čija je struktura već poznata. Ovde predstavljamo kristalnu strukturu antitoksin- toksin kompleksa ez(234stop) gde je molekul toksičnog proteina z skraćen sa 284 aminokiselina na 233, sa strane njegovog C-terminala. Pokazali smo da ovaj nedostajući C-terminal, koji se sastoji od heliks-turn-heliks motiva, iako nije deo ATP vezujućeg džepa, je bitan za funkciju toksina u *E. coli*. Sačinili smo konstrukt ove ne toksične varijante i uspešno je proizveli u ćelijama *E. coli* bez antitoksina e. Kristalizacija je ipak bila uspešna samo nakon formiranja antitoksin- toksin kompleksa. Plazmid pSM19035 [1], je plazmid niskog broja kopija u bakterijskim ćelijama i veoma je rasprostranjen između raznih sojeva bakterija. Proteini zaduženi za njegovo stabilno održavanje u ćelijama bakterija kodirani su u dva regiona. Drugi region, segB, kodira četiri proteina, među njima antitoksin e i toksin z. Efekti toksina na ćeliju domaćina se ispoljavaju kada ćelija domaćin (u toku ćelijske deobe) ostane bez plazmida koji kodira toksin z i njegov antitoksin e, te usled manje stabilnosti antitoksina u odnosu na toksin, toksin preuzima primat i uništava ćeliju domaćina.

Struktura ove varijante kompleksa je određena MR metodom koristeći postojeći model punog ez kompleksa [2] kao polazni model. Sakupljeni su difrakcioni setovi za nativni kompleks do rezolucije od 2,50 Å. Redukcija podataka i skaliranje izvršeno je pomoću programa Denzo i Scalepack, molekularna zamena je izvršena u programu PHASER a utačnjavanje strukture pomoću programa CNS.

[1] Alonso, J. C., Balsa, D., Cherny, I., Christensen, S. K., Francuski, D., Gazit, E., et al. (2007). Bacterial Toxin-Antitoxin Systems as Targets for the Development of Novel Antibiotics. In R. A. Bonomo, & M. E. Tolmasky (Eds.), *Enzyme-Mediated Resistance to Antibiotics: Mechanism, Dissemination, and Prospects for inhibition* (pp. 313-329). Washington, D.C.: ASM Press.

[2] Meinhart, A., Alonso, J. C., Sträter, N. and Saenger, W. (2003). Crystal Structure of the Plasmid Maintenance System e/z: Functional Mechanism of Toxin z and Inactivation by e_2z_2 Complex Formation. Proc. Natl. Acad. Sci. (US) **100:** 1661-1666.



Slika 1. Heterotetramerni kompleks antitoksina e (predstavljen u svetlo sivim nijansama) i toksina z (crn)

CRYSTALLOGRAPHIC STUDY OF GEOMETRY OF Ch/O INTERACTIONS BETWEEN NUCLEIC BASES AND WATER MOLECULE

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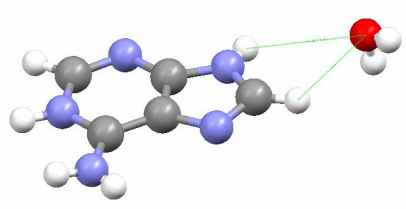
CH/O interactions are one of the most important noncovalent interactions in nature, especially in biopolymer structures. It was shown that CH/O interactions constitute 20–25% of the total number of hydrogen bonds in proteins and play an important role in stabilizing structures of proteins.[1] These interactions also play an important role in crystal engineering and in the recognition of host–guest systems.[2] In our previous work, we performed systematic study of the CH/O interactions between aromatic CH groups and different acceptors.[3] Results showed that the aromatic C-H donors do not show strong preference for linear contacts and that the preference for linear contact depends on the type of the atom or group in *o*-position to the interacting C-H group.

In this work, we performed crystallographic study of geometry of CH/O interactions formed between C-H groups from nucleic bases and oxygen atom from water molecule. Study was performed by analyzing data archived in the Cambridge Structural Database (CSD). Crystal structures containing adenine, timin, guanine, cytosine, uracile and water molecule were screened for intermolecular contacts.

The results of crystallographic analysis showed that C-H fragments from nucleic acids do not show clear preference for linear contacts with oxygen atom from water. This is in agreement with our previous results for CH/O interactions of aromatic CH groups. These conclusions could be very important for recognizing CH/O interactions in biomolecules containing nucleic bases.



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[2] G. R. Desiraju, Chem. Commun., (2005), 2995-3001
[3] D. Ž.Veljković, G. V. Janjić, S. D. Zarić, CrysEngComm, 13 (2011), 5005-5010

КРИСТАЛОГРАФСКО ИСПИТИВАЊЕ ГЕОМЕТРИЈЕ Ch/O ИНТЕРАКЦИЈА ИЗМЕЂУ НУКЛЕИНСКИХ БАЗА И МОЛЕКУЛА ВОДЕ

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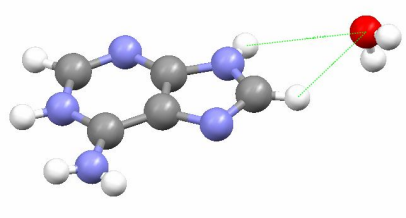
CH/O интеракције представљају једне од најзначајнијих нековалентних интеракција у природи, посебно у структурама биополимера. Доказано је да CH/O интеракције чине 20–25% од укупног броја водоничних веза у протеинима, као и да имају значајну улогу у стабилизовању структура протеина.[1] Ове интеракције такође имају важну улогу у кристалном инжењерству и у препознавању система домаћин-гост.[2] У нашем претходном раду испитивали смо CH/O интеракције између C-H група ароматичних молекула и различитих типова акцептора.[3] Резултати су показали да ароматични C-H донори не показују јасну тежњу ка грађењу линеарних контаката и да та тежња зависи од типа атома или групе у *o*-положају у односу на интерагујућу C-H групу.

У овом раду урађено је кристалографско испитивање геометрије CH/O интеракција између C-H група нуклеинских база и атома кисеоника из молекула воде. Урађена је анализа података добијених из Кембричке банке кристалографских података (CSD). Кристалне структуре које садрже аденин, тимин, гуанин, цитозин, урацил и молекул воде претражене су у циљу проналажења интермолекулских интеракција.

Резултати анализе кристалографских података су показали да C-H фрагменти из нуклеинских база немају јасну тежњу ка грађењу линеарних контаката са кисеоником из молекула воде. Ово је у складу са нашим претходним резултатима за геометрију CH/O интеракција ароматичних CH група. Изведени закључци могу бити од великог значаја за препознавање CH/O интеракција у биолошким молекулима који садрже нуклеинске базе.



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[2] G. R. Desiraju, Chem. Commun., (2005), 2995-3001
[3] D. Ž.Veljković, G. V. Janjić, S. D. Zarić, CrysEngComm, 13 (2011), 5005-5010

SIGNIFICANCE OF THE IN-SITU XRD STUDY OF THE ACTIVE ELECTRODE MATERIALS DURING BATTERY CYCLING

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One of the most important factors that determine the overall battery performance are the electrode materials in the contact with electrolyte and their structural evolution upon cycling. During the charge and discharge procedure, electrode surface and in some batteries-complete electrode material exhibits constant structural changes. Transition into new crystalline phases or even partial amorphisation, crystallite growth and introduction of defects into the crystal structure of electrode can influence the battery efficiency and working life. Thus the study of such changes is essential for further successful battery development. As a natural choice and one of the most efficient ways to investigate fast structural changes during battery cycling is the in-situ XRD technique.
In this study we present the formation of the crystalline phases of anglesite ($PbSO_4$) and lead dioxide (PbO_2) during the anodic oxidation of pure lead in 1 molar sulphuric acid (H_2SO_4). The change of the phase composition during the electrochemical reaction was observed by non-destructive in-situ grazing incidence angle X-ray diffraction (GIXD) method (Figure 1).

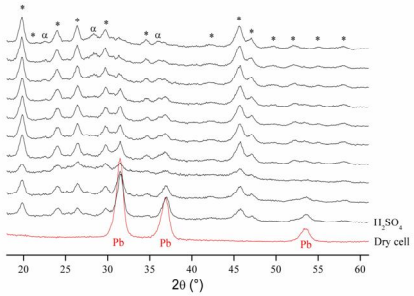

Figure 1. Results of the consecutive in-situ XRD measurements during battery cycling

The observed diffraction peaks of $PbSO_4$ phase are indicated by asterisks "*", the Pb peaks are indicated by the symbol "Pb" and the positions of the α-PbO_2 peaks are denoted by "α". Quantification of the relative phase contents as well as the crystallite size determination were done by Rietveld refinement procedure.

[1] P. Angerer, R. Mann, A. Gavrilović, G. E. Nauer, Materials Chemistry and Physics 114 (2009) 983-989

ZNAČAJ IN-SITU XRD ANALIZE U ISPITIVANJU AKTIVNOG MATERIJALA ELEKTRODE TOKOM CIKLUSA BATERIJE

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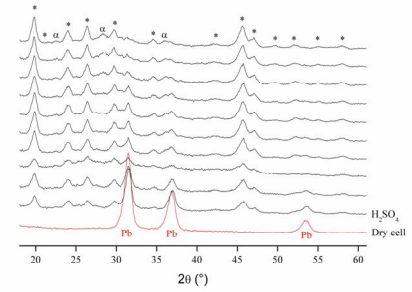
Jedan od najvažnijih faktora koji određuju ukupan rad baterije jesu materijali elektroda u kontaktu sa elektrolitom i njihova strukturna evolucija u toku ciklusa baterije. Tokom procedure punjenja i pražnjenja, površina elektrode, a u nekim baterijama i celokupan materijal elektrode prolaze kroz neprestane strukturne promene. Prelazak u nove kristalne faze, ili čak delimična amorfizacija, rast kristalita i pojava defekata u kristalnoj strukturi elektrode mogu uticati na produktivnost i radni vek baterije. Iz tog razloga je izučavanje takvih promena od suštinskog značaja za dalje unapređenje baterija. Kao logičan izbor i jedan od najefikasnijih načina za izučavanje brzih strukturnih promena u toku ciklusa baterije jeste in-situ XRD metoda.
U ovom radu opisano je formiranje kristalnih faza anglezita ($PbSO_4$) i olovo-dioksida (PbO_2) u toku anodne oksidacije čistog olova u jednom molu sumporne kiseline (H_2SO_4). Promena sastava kristalnih faza u toku elektrohemijske reakcije praćena je pomoću ne-destruktivne in-situ rendgenske metode sa malim upadnim uglom X-zraka (GIXD), (slika).



Slika 1. Rezultati uzastopnih in-situ XRD merenja u toku ciklusa baterije.

Difrakcioni maksimumi koji odgovaraju $PbSO_4$ fazi obeleženi su zvezdicom „*“, pikovi olova obeleženi su kao „Pb“ a difrakcioni pikovi koji odgovaraju α-PbO_2 kristalnoj fazi obeleženi su simbolom „α“.
Kvantitativna analiza relativnih faznih udela kao i veličine kristalita određene su pomoću metode Ritveldovog utačnjavanja.

[1] P. Angerer, R. Mann, A. Gavrilović, G. E. Nauer, Materials Chemistry and Physics 114 (2009) 983-989

CRYSTAL STRUCTURES OF SOME FERROCENE CONTAINING MANNICH BASIS

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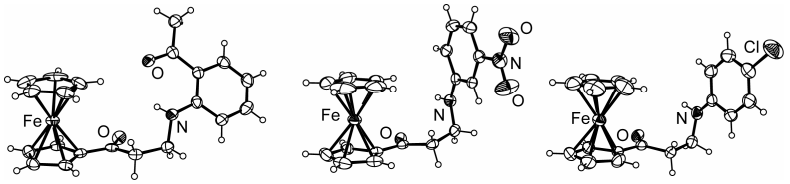
A successful aza-Michael addition of different arylamines to a conjugated enone, acryloylferrocene, has been achieved by ultrasonic irradiation of the mixture of these reactants and the catalyst – montmorillonite K-10. Apart from the excellent yields, the most of the synthesized Mannich basis (3-(arylamino)-1-ferrocenylpropan-1-ones) were crystal substances, suitable for X-ray crystal structure analysis. [1,2] In the last year we were able to analyze 13 compounds of this type. As expected, the synthesized Mannich basis differ in the type of substituents ($-CH_3$, $-F$, $-Cl$, $-C(O)CH_3$ or $-NO_2$) and their position (*ortho*, *meta* or *para*) on arylamino moieties. The structural analysis showed that in all derivatives the cyclopentadienyl rings of ferrocene adopt a nearly eclipsed geometry. Depending on the position of the substituent on the arylamino moiety the monosubstituted 3-(arylamino)-1-ferrocenylpropan-1-ones display two type of conformations. The Mannich basis containing the *meta*- and *para*-substituted arylamino moieties have similar "bent" conformation which is further reflected in the similar manner of their crystal arrangement. The Mannich basis containing the *ortho*-substituted arylamino moiety show unique "extended" conformation and significantly different crystal arrangement with respect to the *meta*- and *para*-derivatives. Despite the pronounced conformational similarities of compounds within the group, the presence of the flexible aliphatic substituents on the Fc units allows the fine structural flexibility of present Mannich basis, thus in the case of the 1-Ferrocenyl-3-(3-nitrophenylamino)propan-1-one we have found two polymorphic forms, both crystallizing in *P*-1 space group. To summarize and compare the intermolecular interactions present in the crystal packing of the analyzed Mannich basis we also employed the Hirshfeld surfaces based tools.



[1] I. Damljanovic et al. J. Organomet. Chem., 696 (2011), 3703-3713.
[2] A. Pejovic et al. Helv.Chim.Acta, accepted for publication, (2012).

KRISTALNE STRUKTURE NEKIH MANIHOVIH BAZA SA FEROCENOM

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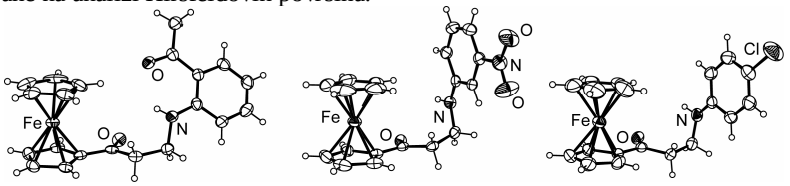
Uspešna aza-Majklova adicija različitih arilamina na konjugovani enon akriloilferocen ostvarena je ultrasoničnim tretiranjem smeše ovih reaktanata i katalizatora – montmorilonita K-10. Pored dobrih prinosa, većina sintetisanih Manihovih baza (3-(arilamino)-1-ferocenilpropan-1-ona) dala je monokristale pogodne za rendgensku strukturnu analizu. [1,2] Tokom prošle godine bili smo u mogučnosti da analiziramo 13 jedinjenja ovog tipa. Kao što se očekivalo, sintetisane Manihove baze se razlikuju u tipu suptituenta (−CH_3, −F, −Cl, −$C(O)CH_3$ ili −NO_2) i njihovom položaju (*orto*, *meta* ili *para*) na arilamino fragmentu. Strukturna analiza je pokazala da u svim derivatima ciklopentadienilni prstenovi ferocena imaju eklipsnu geometriju. U zavisnosti od položaja supstituenata na arilamino fragmentu mosnosupstituisani 3-(arilamino)-1-ferocenilpropan-1-oni imaju dva tipa konformacija. Manihove baze sa *meta*- i *para*-supstituisanim arilamino fragmentima imaju sličnu "savijenu" konformaciju što se dalje odražava u sličnom kristalnom pakovanju molekula ovih baza. Manihove baze sa *orto*-supstituisanim arilamino fragmentom imaju drugačiju "istegnutu" konformaciju i značajno drugačije kristalno pakovanje u odnosu na *meta*- i *para*-derivate. Uprkos naglašenoj konformacionoj sličnosti unutar grupe prisustvo fleksibilnog alifatičnog supstituenta na ferocenskoj jedinici omogućava finu stukturnu fleksibilnost Manihovih baza, tako je u slučaju 1-ferrocenil-3-(3-nitrofenilamino)propan-1-ona utvrđeno postojanje dve plimorfne strukture, koje kristališu u prostornoj grupi *P*-1. Za sumiranje i poređenje inermolekulskih interakcija prisutnih u kristalnim pakovanjima Manihovih baza takođe smo primenili metode zasnovane na analizi Hiršfeldovih površina.



[1] I. Damljanovic et al. J. Organomet. Chem., 696 (2011), 3703-3713.
[2] A. Pejovic et al. Helv.Chim.Acta, accepted for publication, (2012).

PM6 SEMI-EMPIRICAL QUANTUM MECHANICS-ASSISTED DETERMINATION OF THE GEOMETRY AND BINDING ENERGY OF HEME-INTERACTING CYP19A1 AROMATASE INHIBITORS

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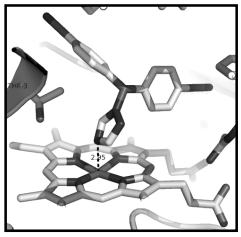
Aromatase (CYP19A1) is a heme-containing cytochrome P450 enzyme which converts androgens to estrogens. The majority of breast cancers are estrogen-sensitive, and inhibition of estrogen synthesis slows tumor growth. Aromatase inhibitors (AIs) are clinically used for treatment of breast cancer in post-menopausal women, and identification of new AIs is necessary because of AI-resistant tumors and the need for AIs with reduced side-effects. Determination of the structural basis of aromatase/AI interactions can guide synthesis of AIs. Although the structure of human aromatase has been solved, no structure exists of aromatase in complex with any AI [1]. Therefore, prediction of the geometry and binding energy of aromatase-AI complexes is essential for structure-based drug design. Molecular docking predicts the binding orientation and affinity of a ligand for a receptor. We conducted comparative analysis of 3 commonly used molecular docking programs: Autodock 4.2, Swissdock and Autodock Vina. Current docking programs appear to have difficulties reproducing heme-ligand interactions [2]. To address this, we applied PM6 semi-empirical quantum mechanics (MOPAC2009) to calculate ligand/receptor partial charges [3,4]. We report optimization of a PM6-assisted protocol for heme-containing receptor docking. Our method was validated on cholesterol 24 hydroxylase (CYP46A1**)**, a structural homolog of CYP19A for which structures have been solved in complex with heme-interacting ligands [5]. We observed significant improvements between calculated and experimental binding geometries for CYP46A1. Application of our method to aromatase significantly improves recovery of AI ligands in proper orientation for interaction with the heme iron. The proposed method is applicable to any metalloprotein-ligand interaction.



[1] D Ghosh, J Griswold, M Erman, W Pangborn, Nature 457 (2009), pp. 219-23
[2] UF Röhrig, A Grosdidier, V Zoete, O Michielin, J Comp Chem. 30 (2009), pp. 2305-15
[3] Z Bikadi, E Hazai, J Cheminform. (2009), pp. 1-15
[4] JJ Stewart, J Mol Model. 15 (2009), pp. 765-805
[5] N Mast, C Charvet, IA Pikuleva, CD Stout, J Biol Chem. 285 (2010) pp. 31783-95

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ODREĐIVANJE GEOMETRIJE I ENERGIJE VEZE U INTERAKCIJI AROMATAZE CYP19A1 SA INHIBITORIMA AROMATAZE, KORIŠĆENJEM PM6 POLU-EMPIRIJSKE KVANTNE MEHANIKE

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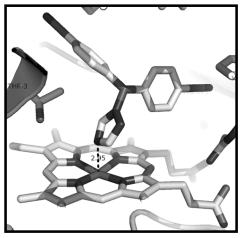
Aromataza (CYP19A1) je citohrom P450 enzim koji sadrži hem i koji konvertuje androgene u estrogene. Većina karcinoma dojke je osetljiva na estrogen, i inhibicijom sinteze estrogena usporava se rast tumora. Inhibitori aromataze (AI) klinički se koriste za lečenje raka dojke u post-menopauzi, a identifikacija novih AI neophodna je zbog AI-rezistentnih tumora i potrebe za smanjenjem neželjenih efekata. Određivanje strukturne osnove aromataza/AI interakcije može da posluži kao vodič za sintezu novih AI. Iako je



struktura humane aromataze rešena, ne postoji struktura aromataze u kompleksu sa AI [1]. Dakle, predviđanje geometrije i energije veze aromataza-AI kompleksa je od suštinskog značaja za dizajniranje boljih lekova. Molekularni doking predviđa orijentaciju i afinitet vezivanja liganda za receptor. Mi smo sproveli komparativnu analizu tri najčešće korišćena programa za molekularni doking: Autodock 4, Swissdock i Autodock Vina. Doking programi koji su u upotrebi imaju teškoće sa reprodukovanjem hem-ligand interakcije [2]. Zbog toga smo primenili PM6 polu-empirijsku kvantnu mehaniku (MOPAC2009) za izračunavanje parcijalnih naelektrisanja liganda i receptora [3,4]. Ovde prikazujemo optimizaciju PM6 doking protokola za receptore koji sadrže hem. Naš metod je potvrđen na holesterol-24-hidroksilazi (CYP46A1), strukturnom homologu CYP19A čija je struktura rešena u kompleksu sa ligandima koji vezuju hem [5]. Videli smo značajna poboljšanja između izračunatih i eksperimentalnih geometrija vezivanja za CYP46A1. Primena ovog metoda na aromatazu značajno je poboljšala identifikaciju AI liganda sa ispravnom orijentacijom u interakciji sa jonom gvožđa iz molekula hema. Predloženi metod je primenljiv na bilo koju interakciju metaloproteina sa ligandom.

[1] D Ghosh, J Griswold, M Erman, W Pangborn, Nature 457 (2009), str. 219-23
[2] UF Röhrig, A Grosdidier, V Zoete, O Michielin, J Comp Chem. 30 (2009), str. 2305-15
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[4] JJ Stewart, J Mol Model. 15 (2009), str. 765-805
[5] N Mast, C Charvet, IA Pikuleva, CD Stout, J Biol Chem. 285 (2010) str. 31783-95

* Zahvaljujemo se Ministarstvu prosvete i nauke, Republike Srbije na finansiranju (Projekat ON172021)

BINUCLEAR PHTHALATO MANGANESE(II) COMPLEX WITH 2,2'-DIPYRIDYLAMINE, $[Mn_2(C_8H_4O_4)_2(C_{10}H_9N_3)_2(H_2O)_2]_n$

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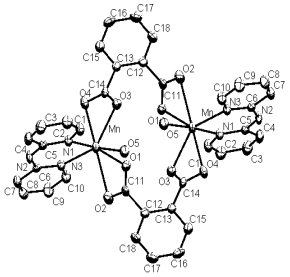
Ternary manganese(II) complexes containing aromatic dicarboxylato and diamine ligands have fascinating crystal structures [1]. As a continuation of our research on design and synthesis of transition metal complexes [2], a novel titled Mn(II) complex has been prepared.

The starting mixture of $Mn(CH_3COO)_2{\cdot}4H_2O$, 2,2'-dipyridylamine (dipya), phthalic acid (H_2pht) and NaOH (molar ratio of 1:2:1:2, respectively) and H_2O was treated in a Teflon-lined steel autoclave at t = 140 °C for 5 days, yielding the title complex. To the best of our knowledge, the obtained complex is the first example among aromatic dicarboxylato Mn(II) complexes with seven-coordinated Mn(II) ions.

Mn(II) ions in the centrosymmetric binuclear unit (Fig. 1) have pentagonal-bipyramidal geometry. There are also two intramolecular hydrogen bonds making a deformed Mn_2O_6 cubane-like core. The aromatic rings of two pht^{2-} ions are almost parallel with dihedral angle of only 1.81 º, while pht^{2-} rings and dipya are nearly perpendicular with dihedral angles of 84.24 and 83.36 º. By intermolecular hydrogen bonds the binuclear units are packed in layers parallel to the *ac*-plane (Fig. 2). The layers are stacked by π-π interactions between dipya ligands belonging to adjacent layers (*Cg*···*Cg* distance about 3.7 Å) resulting in formation of 3D framework.



Crystal data: $C_{36}H_{30}Mn_2N_6O_{10}$, M_r = 816.54, triclinic, space group *P1*, a = 8.3607(5), b = 9.1259(7), c = 11.8551(10) Å, α = 69.307(8), β = 77.471(6), γ = 79.893(6) º, V = 821.18(11) Å^3, Z = 1, F(000) = 418, ρ_x = 1.651g cm^{-3}, μ(Mo Kα) = 0.842 mm^{-1}. The refinement on F^2 (253 parameters) yielded R_1 = 0.062, wR_2 = 0.082, S = 1.08 for all data, and R_1 = 0.044 for 2509 observed reflections with $I \geq 2\sigma(I)$.

Figure 1. The bunuclear unit of $[Mn_2(C_8H_4O_4)_2(C_{10}H_9N_3)_2(H_2O)_2]_n$

[1] C. B. Ma, M. Q. Hu, H. Chen, M. Wang, C. X. Zhang, C. N. Chen, Q. T. Liu, Cryst. Eng. Comm, 12 (2010), 1467–1473; J.-M. Yang, Z.-H. Zhou, H. Zhang, H.-L. Wan, S.-J. Lu, Inorg. Chim. Acta, 358 (2005), 1841–1849.
[2] J. Rogan, D. Poleti, Lj. Karanović, Acta Crystallogr., C67 (2011), m230–m233.

BINUKLEARNI FTALATO MANGAN(II)-KOMPLEKS SA 2,2'-DIPIRIDILAMINOM, $[Mn_2(C_8H_4O_4)_2(C_{10}H_9N_3)_2(H_2O)_2]_n$

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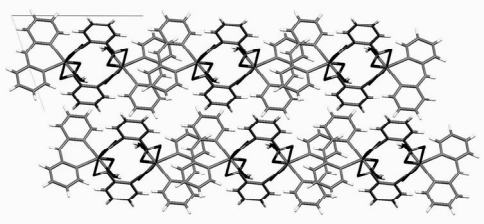
Kompleksi mangana(II) koji sadrže aromatične dikarboksilato i diaminske ligande imaju fascinantne kristalne strukture [1]. Novi Mn(II)-kompleks rezultat je nastavka naših istraživanja na dizajnu i sintezi kompleksa prelaznih metala [2].

Početna smeša $Mn(CH_3COO)_2{\cdot}4H_2O$, 2,2'-dipiridilamina (dipya), ftalne kiseline (H_2pht) i NaOH (u molskom odnosu 1:2:1:2) i H_2O zagrevana je 5 dana na t = 140 °C u čeličnom autoklavu obloženom teflonom, pri čemu je dobijen navedeni kompleks. Prema našim saznanjima, nastali kompleks predstavlja prvi primer među aromatičnim dikarboksilato Mn(II)-kompleksima u kojem postoje sedmokoordinirani Mn(II)-joni.

U centrosimetričnoj binuklearnoj jedinki (Slika 1), Mn(II)-joni imaju pentagonalno--bipiramidalnu geometriju. Postoje i dve intramolekulske vodonične veze koje grade deformisano Mn_2O_6 jezgro nalik kocki. Aromatični prstenovi iz dva pht^{2-} su gotovo paralelni sa uglom od samo 1,81 º, dok su prstenovi pht^{2-} i dipya skoro normalni sa uglovima od 84,24 i 83,36 º. Preko intermolekulskih vodoničnih veza, binuklearne jedinke se pakuju u slojeve paralelne *ac*-ravni (Slika 2). Slojevi su povezani π-π interakcijama između dipya liganada iz susednih slojeva (*Cg*···*Cg* rastojanje iznosi oko 3,7 Å) gradeći tako 3D mrežu.



Kristalografski podaci: $C_{36}H_{30}Mn_2N_6O_{10}$, M_r = 816,54, triklinični sistem, prostorna grupa *P1*, a = 8,3607(5), b = 9,1259(7), c = 11,8551(10) Å, α = 69,307(8), β = 77,471(6), γ = 79,893(6) º, V = 821,18(11) Å^3, Z = 1, $F(000)$ = 418, ρ_x = 1,651g cm^{-3}, μ(Mo Kα) = = 0,842 mm^{-1}. Utačnjavanje sa F^2 (253 parametra) dalo je R_1 = 0,062, wR_2 = 0,082, S = 1,08 za sve podatke, i R_1 = 0,044 za 2509 refleksija sa $I \geq 2\sigma(I)$.

Slika 2. Projekcija strukture $[Mn_2(C_8H_4O_4)_2(C_{10}H_9N_3)_2(H_2O)_2]_n$ na *bc*-ravan

[1] C. B. Ma, M. Q. Hu, H. Chen, M. Wang, C. X. Zhang, C. N. Chen, Q. T. Liu, Cryst. Eng. Comm, 12 (2010), 1467–1473.; J.-M. Yang, Z.-H. Zhou, H. Zhang, H.-L. Wan, S.-J. Lu, Inorg. Chim. Acta, 358 (2005), 1841–1849.
[2] J. Rogan, D. Poleti, Lj. Karanović, Acta Crystallogr., C67 (2011), m230–m233.

CRYSTAL STRUCTURE OF $[Cu_2L_2(H_2O)_2](SO_4)_2{\cdot}2H_2O$ (L = PYRIDOXAL THIOSEMICARBAZONE)

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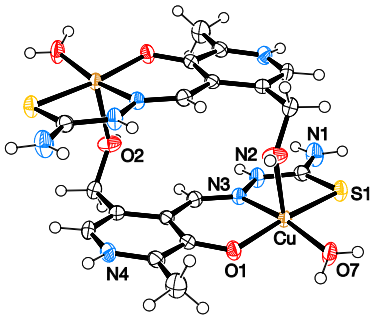
Dark green single crystals of the title complex were prepared by the reaction of slightly acidic (H_2SO_4) methanol solutions of $CuSO_4{\cdot}5H_2O$ and pyridoxal thiosemicarbazone (L) in mole ratio 1:1. Dinuclear complex cation has centrosymmetric structure. The Cu(II) is situated in a square-pyramidal environment ($\tau = 0.04$). The equatorial plane is formed by ligators of ONS coordinated L and one water molecule, while the apical position is occupied by hydroxymethyl oxygen $O(2)^i$ (i = $-x$, $1-y$, $-z$) of the bridging ligand. The Cu atom is shifted towards the apical oxygen atom by 0.173(12) Å. The Cu–atom ligator bond lengths are in the range 1.917(2)–1.967(2) Å for O(1) N(3) and O(7), while Cu–S(1) and $Cu–O(2)^i$ are longer (2.2998(9) Å and 2.233(2) Å, respectively). Pyridoxal thiosemicarbazone is coordinated in neutral, zwitterionic form as tetradentate bridging ligand, *i.e. via* phenol oxygen, hydrazine nitrogen, sulfur and hydroxymethyl oxygen, which, as the bridging ligator, connects the subunits. Such coordination results in formation of two metallocycles, five-membered (thiosemicarbazide) and six-membered (pyridoxilidene). The coordinated ligand slightly deviates from planarity, and dihedral angles between pyridine ring, six- and five-membered metallocycles are 7.54(10)°, 4.80(7)°, respectively. The six-membered metallocycle is in screw-boat conformation and is described by the following puckering parameters: Q = 0.200(2) Å, θ = 67.9(9)°, φ = 34.3(9)°, while the other rings are planar. Crystal structure of the complex is stabilized by an extended inter- and intra-molecular 3D hydrogen-bond network. It can be mentioned that all possible hydrogen donors are involved in hydrogen-bonding, and that sulfate anion acts as multiple hydrogen acceptor.



The data were collected on Gemini S diffractometer (Agilent Technologies) using MoKα radiation (λ = 0.71069 Å), and were corrected for Lorentz, polarization and background effects. The structure was solved by direct methods using SIR92 and refined by full matrix least square methods on F^2 using SHELXL-97 to R = 0.036. *Crystallographic data:* $C_{18}H_{32}Cu_2N_8O_{16}S_4$, M_r = 871.90, monoclinic, space group $P2_1/n$, a = 7.2529(2) Å, b = 11.1766(4) Å, c = 18.8522(6) Å, β = 93.751(3)°, V = 1524.94(8) Å^3, Z = 2, μ(MoKα) = 1.756 mm^{-1}, S = 1.059.

KRISTALNA STRUKTURA $[Cu_2L_2(H_2O)_2](SO_4)_2 \cdot 2H_2O$ (L = TIOSEMIKARBAZON PIRIDOKSALA)

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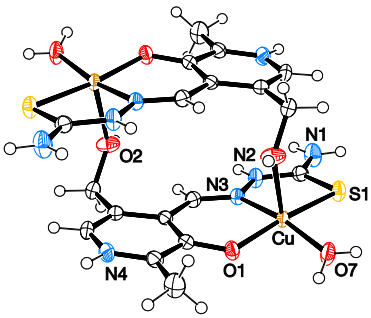
Tamno zeleni kristali naslovljenog kompleksa su dobijeni reakcijom blago zakišeljenih (H_2SO_4) metanolnih rastvora $CuSO_4 \cdot 5H_2O$ i tiosemikarbazona piridoksala (L) u molskom odnosu 1:1. Dinuklearni kompleksni katjon ima centrosimetričnu strukturu. Cu(II) se nalazi u kvadratno-piramidalnom okruženju ($\tau = 0{,}04$) čiju ekvatorijalnu ravan formiraju ligatori ONS koordinovanog L i molekul vode, dok se u apikalnom položaju nalazi atom kiseonika hidroksimetil grupe $O(2)^i$ ($i = -x, 1-y, -z$) susednog molekula liganda, koji ima mostovnu ulogu. Atom Cu odstupa od bazalne ravni i pomeren je za 0,173(12) Å ka apikalnom atomu kiseonika. Dužine veza Cu–atom ligator su u opsegu 1,917(2)–1,967(2) Å za O(1), N(3) i O(7), dok su veze Cu–S(1) i Cu–$O(2)^i$ duže (2,2998(9) i 2,233(2) Å, respektivno). Tiosemikarbazon piridoksala je koordinovan u neutralnoj, cviterjonskoj formi, kao tetradentatni mostovni ligand, tj. preko fenolnog atoma kiseonika, hidrazinskog atoma azota, atoma sumpora i atoma kiseonika hidroksimetil grupe, koji kao mostovni ligator povezuje subjedinice. Na taj način nastaju dva metalocikla, petočlani (tiosemikarbazidni) i šestočlani (piridoksilidenski). Koordinovani ligand blago odstupa od planarnosti, pri čemu su diedralni uglovi između piridinskog prstena, šestočlanog i petočlanog metalocikla 7,54(10)° i 4,80(7)°, respektivno. Šestočlani metalocikl se nalazi u konformaciji „uvijene lađe“ i opisan je sledećim parametrima nabiranja: $Q = 0{,}200(2)$ Å, $\theta = 67{,}9(9)°$, $\varphi = 34{,}3(9)°$, dok su ostali prstenovi planarni. Kristalna struktura kompleksa je stabilizovana razgranatom 3D mrežom inter- i intra-molekulskih vodoničnih veza. Važno je napomenuti da svi potencijalni vodonik-donori učestvuju u građenju vodoničnih veza, pri čemu je sulfatni anjon višestruki vodonik akceptor.



Difrakcioni podaci su prikupljeni na Gemini S difraktometru (Agilent Technologies) korišćenjem MoKα zračenja ($\lambda = 0{,}71069$ Å). Izvršena je korekcija na Lorencov, polarizacioni i efekat pozadinskog šuma. Struktura je rešena direktnom metodom pomoću programa SIR92 i utačnjena metodom najmanjih kvadrata pomoću programa SHELXL-97 do $R = 0{,}036$. *Kristalografski podaci:* $C_{18}H_{32}Cu_2N_8O_{16}S_4$, $M_r = 871{,}90$, monoklinični sistem, prostorna grupa $P\,2_1/n$, $a = 7{,}2529(2)$ Å, $b = 11{,}1766(4)$ Å, $c = 18{,}8522(6)$ Å, $\beta = 93{,}751(3)°$, $V = 1524{,}94(8)$ Å^3, $Z = 2$, μ(MoKα) = 1,756 mm^{-1}, $S = 1{,}059$.

STRONG HYDROGEN BONDS OF COORDINATED WATER. INFLUENCE OF METAL CATION ON WATER HYDROGEN BONDS

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Water plays an essential role in chemical structures and processes in various systems, from materials to biology. Small size and high polarity govern water capabilities and the complexity of its behaviour. Most important is its hydrogen bonding ability, as water forms strong hydrogen bonds to other polar molecules and builds strong networks with itself.[1-3]

In this work the influence of water coordination to a metal cation on water hydrogen bonds was studied by analyzing crystal structures from Cambridge Structural Database and by high level *ab initio* calculations. The hydrogen bonds of the water molecules in the first hydration shell of the cation were compared with the hydrogen bonds of free water molecules. To the best of our knowledge, this is the first work reporting on the strength of the hydrogen bonds of the first hydration shell of metal cations based on the data in the crystal structures from the CSD. Positively charged complexes form quite strong hydrogen bonds, the hydrogen bond energy of $[Zn(H_2O)_6]^{2+}$ complex is -21.89 kcal/mol, which is several times stronger than the hydrogen bond of non-coordinated water, -4.77 kcal/mol.

Hence, the presence of a cation changes remarkably the strength of hydrogen bonds. Moreover, the hydrogen bond of aqua ligand has a strong influence on the stability and coordination number of a complex. The results can be important for all the systems where a water molecule is in contact with metal cations, from biomolecules to materials.

[1] W. M. Latimer, W. H. Rodebush, J. Am. Chem. Soc., 42 (1920), 1419-1433
[2] L. Pauling, J. Am. Chem. Soc., 57 (1935), 2680-2684
[3] M. L. Huggins, J. Org. Chem., 1 (1937), 407-456

JAKE VODONIČNE VEZE KOORDINOVANOG MOLEKULA VODE. UTICAJ JONA METALA NA JAČINU VODONIČNE VEZE

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Voda ima veoma značajnu ulogu u formiranju različitih struktura kao i u brojnim procesima u biološkim sistemima. Svojstva molekaula vode i kompleksno ponašanje posledica su male veličine i visoke polarnosti molekula vode. Jedna od najznačajnijih karakteristika molekula vode je sposobnost vodoničnog vezivanja za druge polarne molekule kao i formiranje mreže vodoničnih veza između samih molekula vode.[1-3]

U ovom radu ispitivan je uticaj koordinacije vode za jon metala na vodonično vezivanje molekula vode, analizom podataka dobijenih iz Kembričke banke kristalografskih podataka kao i *ab initio* proračunima visokog nivoa. Poređena je jačina vodonične veze između koordinovanog i nekoordinovanog molekula vode sa jačinom vodonične veze između dva nekoordinovana molekula vode. Prema našim saznanjima, u ovom radu je po prvi put ispitivana jačina vodoničnih veza koju grade molekuli vode u prvoj koordinacionoj sferi, na osnovu analize kristalnih struktura iz CSD-a. Pozitivno naelektrisani kompleksi formiraju veoma jake vodonične veze. Energija vodonične veze za kompleks $[Zn(H_2O)_6]^{2+}$ iznosi -21,89 kcal/mol, što je nekoliko puta jače od vodonične veze koju grade nekoordinovani molekuli vode (-4,77 kcal/mol).

Dobijeni rezultati jasno ukazuju da prisustvo jona metala značajno utiče na jačinu vodonične veze. Takođe, vodonične veze koje grade koordinovani molekuli vode značajno utiču na stabilnost kompleksa i njegov koordinacioni broj. Ovi rezultati mogu biti od značaja za sve sisteme gde su molekuli vode u kontaktu sa jonima metala, od biomolekula do materijala.

[1] W. M. Latimer, W. H. Rodebush, J. Am. Chem. Soc., 42 (1920), 1419-1433
[2] L. Pauling, J. Am. Chem. Soc., 57 (1935), 2680-2684
[3] M. L. Huggins, J. Org. Chem., 1 (1937), 407-456

POSTER PRESENTATIONS

ПОСТЕРСКА СЕКЦИЈА

STRUCTURAL CHEMISTRY AND SOLID STATE PHYSICS OF Mn(III) SPIN-CROSSOVER COMPOUNDS.

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We study the rare case of Mn(III) complexes with spin transition. A new mononuclear Mn(III) complex, [Mn(5-MeO-salen-N- 1,5,8,12)]ClO_4 was synthesized and characterized by single crystal X-ray diffraction and magnetic measurements. Suitable single crystals are obtained in few days by slowly evaporation from the mother liquor. The X-ray diffraction measurements were done with Rigaku R-AXIS RAPID II at three different temperature 100, 273, 293K. CrystalClear software package was used for data collection and CrystalStructure software package for the structure solution and refinement. The compounds crystallize in a monoclinic crystal system with the space group P2/a. The cell parameter are a = 17.534(6) Å, b = 8.503(3) Å, c = 17.778(6) Å, β = 96.606(5)°, V = 2632.95 Å^3, Z = 4. The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The asymmetric units contain two different cationic mononuclear complexes with the same structure, but with different packing sublattices and supramolecular interactions (hydrogen bonds and π-π stacking). Each complex unit realized with a hexadentate ligands has a pseudo-octahedral geometry with two oxygen atom in the axial positions and four nitrogen atom in the ecuatorial plane. Rising the temperature, the volume cell increase, but the cell parameter dimensions are modified anisotropically, along a axis and less on the other two. Only one unit present low spin to high spin crossover process, the other unit remaining in the high spin state. The spin transition takes place at 250K temperature and is finished near 400K. The subtle balance between molecular and supramolecular interactions determines the dynamics and the cooperativity effects of the lattice in the spin crossover process.

Acknowledgement: This work is supported by the CNCSIS Grant PCCE-9/2010 and bilateral cooperation Romania-China grant, nr. 517/2011.

NEW Co(II) AND Ni(II) CUBAN-LIKE STRUCTURE. STRUCTURAL PROTOTYPES IN COORDINATION CHEMISTRY.

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Polynuclear complexes based on paramagnetic metal ions offer the potential for new technological advances exploiting their magnetical and optical properties. The tetranuclear clusters with a cubane topology represent a distinct class offering case studies for the role of mutual interactions between ions in the circumstance of relatively high effective molecular symmetry. Particularly, when metal ions are able to show magnetic anisotropy, the whole cluster can achieve characteristics of single molecule magnet.

A series of isostructural compounds with cubane like structure, $[ML(MeOH)Br]_4$, L=1-hydroxymethyl, 2,3 dimethyl 4-X pyrazoles (where x=I, NO_2) and M=Co(II),Ni(II), was synthesized and structurally characterized by single crystal X-ray diffraction. The ligands are pyrazoles Mannich bases synthesized from unsubstituted pyrazoles on the nitrogen atom and formaldehyde. The complexation reactions gave two compounds, where the cubane like structure is the main product. Suitable single crystals are obtained in 48h by slowly evaporation from the mother liquor. The X-ray diffraction measurements were done with Rigaku R-AXIS RAPID II at room temperature and CrystalClear software package, the structure solution and refinement with the CrystalStructure software package. The compounds crystallize in a tetragonal crystal system with the space group I41/acd (#142). The cell parameter are a = 14.348(2) Å, c = 50.837(4) Å, V = 10466(3) $Å^3$, Z = 8. The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model.

Acknowledgement: This work is supported by the CNCSIS Grant PCCE-9/2010.

SYNTHESIS, CRYSTAL STRUCTURE AND ANTIPROLIFERATIVE ACTIVITY OF METHYL-2-(5-(4-METHOXYPHENYL)METHYLENE-2-DIOXOTETRAHYDROTHIAZOLE-3-YL)PROPIONATE

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In the research for new antiproliferative agents, a new methyl ester of propionic acid with 2,4-dioxotetrahydrothiazol core has been synthesized. Methyl-2-(5-(4-methoxyphenyl)methylene-2-dioxotetrahydrothiazole-3-yl)propionate has been prepared using Knoevenagel condensation of corresponding aldehyde and thiazolidinedione core, with further nucleophilic substitution with methyl 2-bromo-propionate. The single crystals of suitable size were obtained by recrystallization from an ethanol solution after two weeks in refrigerator.

Compound has been characterized on the basis of FTIR, ^{1}H and ^{13}C NMR spectroscopy and X-ray crystal structure analysis. The molecules are held together by van der Waals forces forming wave-like pseudo-chains along *a*-axis (Figure). The chains are packed in 3D network *via* weak face to face π-π interactions which exist between aromatic rings from adjacent chains [the shortest C–C distance is 3.868(3) Å].

For the first time methyl-2-(5-(4-methoxyphenyl)methylene-2-dioxotetrahydrothiazole-3-yl)propionate has been evaluated against human colon and brest cancer cell lines, HCT–116 and MDA–MB–231, respectively.

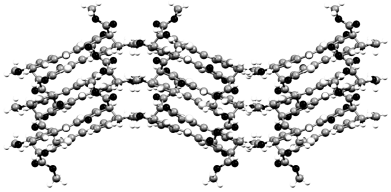

Figure. Crystal packing along *a*-axis (*c*-axis is horizontal)

Crystal data: $C_{15}H_{15}NO_5S$, $M_r = 321.34$, orthorhombic, space group *Pbcn*, $a = 16.7715(4)$, $b = 7.5358(8)$, $c = 24.9575(13)$ Å, $V = 3154.3(4)$ Å^3, $Z = 8$, $F(000) = 1344$, $\rho_x = 1.353$ g cm^{-3}, μ(Mo Kα) = 0.227 mm^{-1}. The refinement on F^2 (207 parameters) yielded $R_1 = 0.061$, $wR_2 = 0.138$, $S = 1.15$ for all data, and $R_1 = 0.053$ for 2653 observed reflections with $I \geq 2\sigma(I)$.

SINTEZA, KRISTALNA STRUKTURA I ANTIPROLIFERATIVNA AKTIVNOST METIL-2-(5-(4-METOKSIFENIL)METILEN-2,4-DIOKSOTETRAHIDROTIAZOL-3-IL)PROPIONATA

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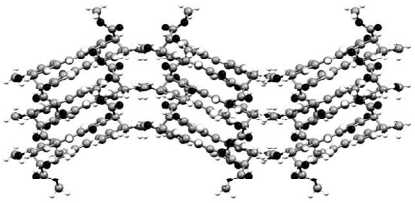
U cilju pronalaženja novih antiproliferativnih agenasa, sintetisan je metil estar propionske kiseline sa 2,4-dioksotetrahidrotiazolskim jezgrom. Knoevenagel-ovom kondenzacijom odgovarajućeg aldehida i tiazolidindionskog jezgra, a zatim nukleofilnom supstitucijom pomoću metil-2-brom-propionata dobijen je metil-2-(5-(4-metoksifenil)metilen-2,4-dioksotetrahidrotiazol-3-il)propionat. Monokristali zadovoljavajućih dimenzija nastali su prekristalizacijom iz etanola posle dve nedelje stajanja u frižideru.

Jedinjenje je okarakterisano FTIR, ^{1}H i ^{13}C NMR spektroskopijom i rendgenskom struktrurnom analizom. Molekuli su povezani van der Valsovim silama gradeći talasaste pseudo-lance duž *a*-ose (slika). Lanci se pakuju u 3D mrežu preko slabih „face to face" $\tilde{\pi}$-π interakcija koje postoje između aromatičnih prstenova susednih lanaca [najkraće C–C rastojanje iznosi 3,868(3) Å].

Prvi put ispitivana je *in vitro* antiproliferativna aktivnost metil-2-(5-(4-metoksifenil)metilen-2,4-dioksotetrahidrotiazol-3-il)propionata prema ćelijskim linijama humanog karcinoma debelog creva, HCT-116, i dojke, MDA-231.



Slika. Prikaz pakovanja duž *a*-ose (*c*-osa je horizontalna)

Kristalografski podaci: $C_{15}H_{15}NO_5S$, $M_r = 321{,}34$, rombični sistem, *Pbcn*, $a = 16{,}7715(4)$, $b = 7{,}5358(8)$, $c = 24{,}9575(13)$ Å, $V = 3154{,}3(4)$ Å^3, $Z = 8$, $F(000) = 1344$, $\rho_x = 1{,}353$ g cm^{-3}, μ(Mo Kα) = 0,227 mm^{-1}. Utačnjavanje sa F^2 (207 parametara) dalo je $R_1 = 0{,}061$, $wR_2 = 0{,}138$, $S = 1{,}15$ za sve podatke, i $R_1 = 0{,}053$ za 2653 refleksije sa $I \geq 2\sigma(I)$

COMPARATIVE ANALYSIS OF THREE MOLECULAR DOCKING PROTOCOLS: A CASE STUDY OF CYP19 P450 AROMATASE INHIBITORS

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A number of rapid, user-friendly molecular docking programs are now freely-available to academic users, enabling researchers from a range of fields to apply molecular docking to study protein-ligand interactions. However, each docking program has different advantages and limitations, and the choice of docking protocol can have significant effects on the results obtained, including: identification of top binders and protein-ligand interaction geometries. Furthermore, each program relies on different methods of estimating protein-ligand interaction energies (ligand binding affinities) and different scoring functions, making comparison of docking results with experimental ligand binding studies difficult. To address these issues, we conducted a comparative analysis of three commonly used molecular docking programs: Autodock 4.2 [1], Swissdock [2] and Autodock Vina [3]. As a case study, we docked different ligand classes to human aromatase (CYP19). Aromatase is a heme-containing P450 enzyme which catalyzes the final step of estrogen synthesis, and represents an important target of breast-cancer chemotherapeutics. Aromatase was chosen as a 'typical' docking problem for this case study, since: diverse small-molecule inhibitors have been identified; a structure of substrate-bound aromatase has been published; and numerous aromatase inhibitor studies have been conducted [4]. In addition, the aromatase ligand binding pocket contains diverse ligand-interacting moieties, including: aromatic residues, heme, hydrogen-bond donors/acceptors, hydrophobic and charged residues. Furthermore, since molecular docking of heme-interacting ligands has been reported to require special consideration, this case study may serve to highlight problems encountered when docking to heme-containing proteins [5]. Each docking program was compared using the following criteria: ease-of-use, speed, customizability, and agreement with experimental evidence.

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*Supported by the Ministry of Education and Science, Republic of Serbia (Project ON172021)

KOMPARATIVNA ANALIZA TRI 'MOLECULAR DOCKING' PROTOKOLA: STUDIJA INHIBITORA CYP19 P450 AROMATAZE

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Veliki broj brzih, korisnički orjentisanih 'molecular docking' programa dostupan je akademskim korisnicima i omogućava istraživačima iz najrazličitijih oblasti proučavanje protein-ligand interakcija. Međutim, svaki od ovih programa ima svoje prednosti i ograničenja a sam izbor protokola može imati velikog uticaja na dobijene rezultate, uključujući identifikaciju najboljih liganda i geometriju interakcije između proteina i liganda. Osim toga, svaki program bazira se na različitoj metodi procene energije interakcije (afiniteta liganda) i različitoj 'score' funkciji, tako da poređenje rezultata sa eksperimentalno dobijenim vrednostima nije jednostavno. Da bi odgovorili na neka od ovih pitanja, sproveli smo komparativnu analizu tri najčešće korišćena programa za 'molecular docking': Autodock 4.2 [1], Swissdock [2] i Autodock Vina [3]. Kao test slučaj posmatrali smo vezivanje različitih klasa liganda za humanu aromatazu (CYP19). Aromataza je protein iz grupe P450 enzima koji sadrži hem i čija je funkcija kataliza poslednjeg koraka u sintezi estrogena, i kao takav predstavlja metu hemioterapeutika u lečenju kancera dojke. Aromataza je izabrana kao 'tipičan' problem obzirom na to da je struktura kompleksa aromataze sa supstratom rešena i objavljena, da su identifikovani brojni mali molekuli inhibitori aromataze i sprovedene studije njihove efikasnosti [4]. Takođe, mesto vezivanja liganda za aromatazu, 'binding pocket', sadrži različite grupe sposobne da interaguju sa ligandom, uključujući aromatične bočne ostatke, hem, donore i akceptore vodoničnih veza, hidrofobne i naelektrisane aminokiselinske bočne ostatke. Obzirom da se u literaturi navodi da su potrebna dodatna razmatranja u slučajevima liganda koji interaguju sa hem grupom, ova studija bi omogućila identifikaciju problema na koje se nailazi u radu sa proteinima koji sadrže hem. [5]. U poređenju programa koristili smo sledeće kriterijume: lakoća korišćenja, brzina, prilagodljivost i slaganje dobijenih rezultata sa eksperimentalno određenim vrednostima.

[1] GM Morris et al., J. Computational Chemistry 19 (1998), pp. 1639-1662
[2] Grosdidier A, Zoete V, Michielin O., Nucleic Acids Res. (2011), pp. W270-7
[3] O Trott, AJ Olson, J. Computational Chemistry 31 (2010), pp. 455-461
[4] D Ghosh, J Griswold, M Erman, W Pangborn, Nature 457 (2009), pp. 219-23
[5] UF Röhrig, A Grosdidier, V Zoete, O Michielin, J Comp Chem. 30 (2009), pp. 2305-15

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CRYSTAL STRUCTURE OF 2-[2--(TRIFLUOROMETHYL)PHENYL]-2*H*-1-BENZOPYRAN-4(3*H*)--ONE

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The title compound belongs to the group of flavanones which occur predominantly in citrus fruits. This compound was obtained by cyclization of chalcones in basic media and is comprised out of a trifluoromethyl-phenyl ring connected to a fused γ-pyranone-phenyl ring by a single C9–C10 bond (Figure 1).

The γ-pyranone ring (C1–C6–C7–C8–C9–O1) adopts an envelope conformation with the chiral carbon atom (C9) standing out of the ring plane. There are no significant hydrogen bonds but the crystal packing is stabilized by two intermolecular interactions of the C–H···O and C–H···F type, as well as a π···π interaction between two nearly parallel phenyls from the fused γ-pyranone-phenyl rings with a perpendicular distance of 3.62 Å.

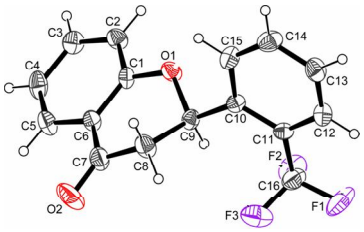

Figure 1. The crystal structure of title compound with atom labels and 30 % probability displacement ellipsoids for non-H atoms. H atoms are represented as small spheres of arbitrary radii.

Crystallographic data: formula $C_{16}H_{11}F_3O_2$, orthorhombic, space group $Pna2_1$, a = 8.2291(9), b = 22.020(3), c = 7.3355(11) Å, V = 1329.2(3) Å^3, Z = 4, μ(Mo $K\alpha$) = 0.12 mm^{-1}, Mo $K\alpha$ radiation. Structure was solved using the SHELXS97 program and was refined by SHELXL97 to a residual R-factor of 8.68 % for 1462 reflections with $I>2\sigma(I)$ and 190 refined parameters.

КРИСТАЛНА СТРУКТУРА 2-[2-(ТРИФЛУОРОМЕТИЛ)ФЕНИЛ]--2*H*-1-БЕНЗОПИРАН-4(3*H*)-ОН

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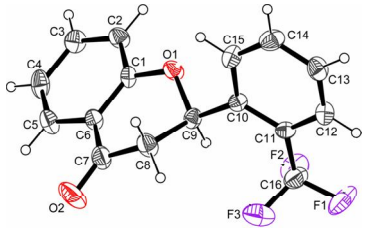
2-[2-(трифлуорометил)фенил]-2*H*-1-бензопиран-4(3*H*)-он (Слика 1) припада групи флаванона који се јављају у плодовима цитруса. Ово једињење је добијено циклизацијом халкона у базној средини градећи γ-пиранон прстен (C1–C6–C7–C8–C9–O1) за који је кондензован фенилни прстен (C1–C2–C3–C4–C5–C6). Ови кондензовани прстенови су путем једноструке везе повезани са трифлуорметил-фенилом преко фенилног C10 и γ-пирановог C9 атома.

Прстен γ-пиранона (C1–C6–C7–C8–C9–O1) је непланаран и има конформацију писма са хиралним атомом угљеника (C9) који одступа од средње равни прстена. У кристалном паковању није нађена ниједна значајна водонична веза, међутим структуру стабилизују две међумолекулске интеракције C–H···O и C–H···F типа, као и једна π···π интеракција која се јавља између два приближно паралелна фенилна прстена (C1–C2–C3–C4–C5–C6) са нормалним растојањем од 3,62 Å.



Слика 1. Кристална структура 2-[2-(трифлуорометил)фенил]-2*H*-1-бензопиран-4(3*H*)--он са ознакама неводоничних атома.

Анизотропни термални елипсоиди су приказани са 30 % вероватноће за све неводоничне атоме, док су H атоми представљени као мале сфере произвољних радијуса. Кристалографски подаци: формула $C_{16}H_{11}F_3O_2$, орторомбични кристални систем, просторна група $Pna2_1$, a = 8,2291(9), b = 22,020(3), c = 7,3355(11) Å, V = 1329,2(3) Å^3, Z = 4, μ(Mo $K\alpha$) = 0,12 mm^{-1}, Mo $K\alpha$ зрачење. Структура је решена помоћу SHELXS97 програма и утачњена програмом SHELXL97 до финалног R-фактора од 8,68 % за 1462 рефлексија са $I>2\sigma(I)$ и 190 утачњаваних параметара.

CRYSTALLOGRAPHY IN XVIII AND XIX CENTURY IN CENTRAL EUROPE

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Mineralogists and crystallographers from Hungary were of great importance, at the end of XVIII and in XIX century. They were equally known for their field work in discovering new minerals and crystal structure determinations of individual minerals and for the improvement in teaching mineralogy and crystallography. Famous mines of gold, silver and copper, such as Schemnitz and *Bystrica*, were placed in the former territory of Hungary. The first lectures and classes of mineralogy, at the academic level, were held at the Mining Academy in Semnic. These experiences are passed on to the territory of Transylvania and Cluz also rich in minerals [1]. The above mentioned institutions stand out for their collections of minerals and systematic view of their crystal structures. The first known mineralogists from former Hungarian region are: Miklós Oláh (1493-1568) [2] and Csibi István (1673-1719) [3]. The first mineralogist from Novi Sad was Stevan Milovanov (1855-1946). Stevan Milovanov started his work in the field of mineralogy in Hungary [4]. He published a textbook, a similar to Hungarian collection, in which he sketched and presented a variety of crystal structures and crystallographic labels.

[1] G. Incze, Ki a tellur igazi felfedezője, Szabad Egyetem III, (1926), str. 19
[2] S. Hóman, Magyar Történelem, Királyi Magyar egyetemi nyomda, (1928), Budapest
[3] J. Szinnyei, Magyar írók élete és munkái II, Caban–Exner, (1893), Hornyánszky, Budapest
[4] S. Milovanov, Fizika u Srba, Srpska štamparija dra Svetozara Miletića, Novi Sad, (1886), str. 1-30

KRISTALOGRAFIJA U XVIII I XIX VEKU U CENTRALNOJ EVROPI

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Mineralozi i kristalografi iz Mađarske su XVIII i XIX veku bili od izuzetnog značaja. Podjednako su bili poznati kako po svom terenskom radu u otkrivaju novih minerala i determinaciji kristalne strukture pojedinih minerala tako i po unapređenju nastave iz mineralogije i kristalografije. Na nekadašnjoj teritoriji Mađarske nalazili su se čuveni rudnici zlata, srebra i bakra, Šemnic (Schemnitz) i Bistrica (*Bystrica*). Prva predavanja o mineralogiji akademskog nivoa održana su na Rudarsko Metalurškoj Akademiju u Šemnicu. Ova iskustva su prenošena na teritorije Transilvanije i Kluža, takođe bogate mineralima [1]. Pomenute ustanove se ističu i po svojim zbirkama minerala i sistematskom prikazu njihovih kristalnih stuktura. Prvi poznatiji mineralozi nekadašnje Mađarske regije su: Mikloš Olah (Oláh Miklós, 1493-1568) [2] i Ištvan Čibe (Csiba István, 1673-1719) [3]. Prvi novosadski mineralog je Stevan Milovanov (1855-1946), koji je svoj rad u oblasti mineralogije otpočeo u Mađarskoj [4]. Objavio je udžbenik, sličan mađarskoj zbirci, koji je sam skicirao i predstavio je razne kristalne strukture i kristalografske oznake.

[1] G. Incze, Ki a tellur igazi felfedezője, Szabad Egyetem III, (1926), str. 19
[2] S. Hóman, Magyar Történelem, Királyi Magyar egyetemi nyomda, (1928), Budapest
[3] J. Szinnyei, Magyar írók élete és munkái II, Caban–Exner, (1893), Hornyánszky, Budapest
[4] S. Milovanov, Fizika u Srba, Srpska štamparija dra Svetozara Miletića, Novi Sad, (1886), str. 1-30

POSSIBLE TYPES OF ELECTRICAL CONDUCTIVITY OF NANOCRYSTALLINE In-DOPED ZINC FERRITES

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This study presents results concerning on dielectric behavior, conductivity and some magnetic properties of the nanosized $Zn_{1-x}In_xFe_2O_4$ powders (x = 0, 0.15, 0.2, and 0.3), obtained by coprecipitation method. The nanocrystalline In-doped zinc ferrites were characterized by X-ray analysis, TEM and measurements of specific surface area. The frequency dependance of the dielectric permittivity and the conductivity of the samples are determined in the frequency range ($1\text{-}10^5$) Hz, at temperatures from 300 to 350 K. The AC conductivity was found to follow universal dielectric response $\sigma_{ac}(\omega,T) = A(T)\cdot\omega^{n}(T)$. Analyzing the variation of the parameter *n* with the temperatures, we discuss the possible conduction mechanism in investigated samples.

TIPOVI ELEKTRIČNE PROVODLJIVOSTI NANOKRISTALNIH INDIJUMOM DOPIRANIH CINK FERITA

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Ovaj rad predstavlja rezultate ispitivanja dielektričnog ponašanja, provodljivosti i nekih magnetnih osobina nanoprahova sastava $Zn_{1-x}In_xFe_2O_4$ (x = 0, 0.15, 0.2, i 0.3) dobijenih metodom taloženja. Nanokristalna struktura indijumom dopiranih cink ferita je potvrđena difrakcijom x-zraka, transmisionom elektronskom mikroskopijom i određivanjem veličine zrna. Frekventna zavisnost dielektrične konstante i provodljivosti uzoraka je određena u frekventnom opsegu ($1\text{-}10^5$) Hz i pri temperaturama od 300 K do 350 K. Utvrđeno je da provodljivost podleže zakonitosti $\sigma_{ac}(\omega,T) = A(T)\cdot\omega^n(T)$. Analizirajući zavisnost parametra *n* od temperature, diskutovani su mogući mehanizmi provođenja u ispitivanim uzorcima.

X-RAY DIFFRACTION ANALYSIS OF *N*-ISOPROPYLACRYLAMIDE-*co*-2-HYDROXYPROPYL METHACRYLATE HYDROGELS

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Hydrogels are networked hydrophilic polymers which have the ability to absorb large amounts of water or biological fluids, where they do not dissolve, but swell, while maintaining a three-dimensional structure. Swollen hydrogels possess soft, elastic consistency, which resemble to the living tissue more than any other class of synthetic biomaterials [1, 2]. Poly(N-isopropylacrylamide), pNIPAM, is a typical representative of the thermo-sensitive polymers, from the group of "intelligent gels", which is usually copolymerized with a certain amount of comonomer to obtain the desired properties of the hydrogels.

The aim of this study was to obtain information by X-ray diffraction analysis on the structure of copolymeric hydrogels of poly(*N*-isopropylacrylamide-*co*-2-hydroxypropyl methacrylate), p(NIPAM-HPMet). Synthesis of hydrogels was carried out by radical polymerization of N-isopropylacrylamide comonomer with 5, 10, 15 and 20 mol.% 2-hydroxypropyl methacrylate and with 1, 2 and 3 mol.% ethylene glycol dimethacrylate as crosslinker in acetone at the temperature of 70-85 °C. Homopolymer pNIPAM was synthesized with 2 mol.% of crosslinker under the same reaction conditions. The synthesized hydrogels were converted into the xerogel state and grounded into the powder. The XRD patterns were recorded at the Phillips PW1030 diffractometer with CuK_{α} monochromatic radiation, wavelength $\lambda = 1.54178$ Å. Samples were recorded in the angle range $2\theta = 7 - 60$ °, with step 0.05 ° and recording time, $\tau = 5$ s. The empirical method for assessing the crystallinity degree through the crystallinity index (CrI) has applied [3].

The results of X-ray diffraction analysis indicate that synthesized copolymers p(NIPAM-HPMet) have the semi-crystalline, amorphous-crystalline structure. The results have also shown the decrease in crystallinity by introducing HPMet in the structure of the hydrogel.

[1] N.A. Peppas, P. Bures, W. Leobandung, H. Ichikawa, Eur. J. Pharm. Biopharm., 50 (2000) 27–46.
[2] Y. Qiu, K. Park, Adv. Drug Delivery Rev., 53 (2001) 321–339.
[3] L. Segal, C.M. Conrad, American Dyestuff Reporter, 46 (1957) 637–642.

RENDGENSKA DIFRAKCIONA ANALIZA HIDROGELOVA *N*-IZOPROPILAKRILAMID-*ko*-2 HIDROKSIPROPILMETAKRILATA

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Hidrogelovi su umreženi hidrofilni polimeri koji imaju sposobnost da apsorbuju velike količine vode ili bioloških fluida, pri čemu se ne rastvaraju, već bubre, zadržavajući trodimenzionalnu strukturu. Nabubreli hidrogelovi imaju meku, elastičnu konzistenciju, zbog čega podsećaju na živa tkiva više nego bilo koja druga klasa sintetičkih biomaterijala [1, 2]. Poli(N-izopropilakrilamid), pNIPAM, je tipičan predstavnik temperaturno osetljivih polimera, iz grupe „inteligentnih gelova", koji se obično kopolimerizuje sa određenom količinom komonomera u cilju dobijanja željenih svojstava hidrogelova.

Cilj rada je bio da se rendgenskom difrakcionom analizom dobiju informacije o strukturi kopolimernih hidrogelova poli(*N*-izopropilakrilamid-*ko*-2-hidroksipropilmetakrilata), p(NIPAM-HPMet). Hidrogelovi su sintetisani radikalnom polimerizacijom komonomera *N*-izopropilakrilamida sa 5, 10, 15 i 20 mol.% 2-hidroksipropilmetakrilata i molskim odnosima umreživača 1, 2 i 3 mol.% etilenglikoldimetakrilata u acetonu, na temperaturi 70-85 °C. Homopolimer p(NIPAM) je sintetisan sa 2 mol.% umreživača pod istim reakcionim uslovima. Sintetisani hidrogelovi su prevedeni u stanje kserogelova, samleveni, i u obliku praha ispitivani su na difraktometru Phillips PW1030 sa monohromatskim CuK_α zračenjem talasne dužine λ = 1,54178 Å. Uzorci su snimani u intervalu 2θ = 7 – 60 °, sa korakom 0,05 ° i vremenom zadržavanja, τ = 5 s. Primenjena je empirijska metoda za procenu stepena kristaliničnosti preko indeksa kristaliničnosti (CrI) [3].

Rezultati rendgenske difrakcione analize sintetisanih kopolimera p(NIPAM-HPMet)-a ukazuju na semikristaliničnu, tj. amorfno-kristalnu strukturu i na smanjenje kristaliničnosti uvođenjem HPMet-a u strukturu hidrogela.

[1] N.A. Peppas, P. Bures, W. Leobandung, H. Ichikawa, Eur. J. Pharm. Biopharm., 50 (2000) 27–46.
[2] Y. Qiu, K. Park, Adv. Drug Delivery Rev., 53 (2001) 321–339.
[3] L. Segal, C.M. Conrad, American Dyestuff Reporter, 46 (1957) 637–642.

SYNTHESIS AND CRYSTAL STRUCTURE OF 3E,6E-DIHYDROXIMINO-17-OXA-D-HOMOANDROST-4-EN-16-ON

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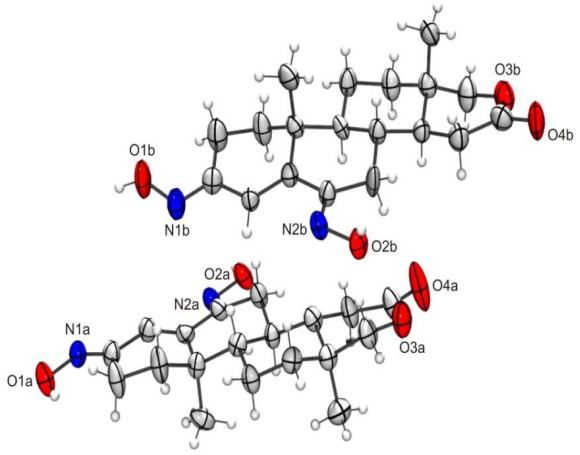
In multistage synthesis, starting from dehydroepiandrosterone a new compound 3E,6E-dihydroximino-17-oxa-D-homoandrost-4-en-16-on with potential biological activity is obtained. Structure of newly synthesized compound was confirmed by spectroscopic data (IR, ^{1}H-NMR, ^{13}C-NMR) and X-ray analysis.



Crystallographic data for compound were collected at room temperature on an Oxford Diffraction Gemini S system using MoKα radiation (λ = 0.7107 Å). The program suite CrysAlis^{Pro} [1] was used for data collection, semi-empirical absorption correction and data reduction. Structure was solved with direct methods using SIR97 [2] and was refined by full-matrix least-squares methods on F^2 with SHELXL-97 [3].

Slika 1. A view of molecular structure of $C_{19}N_2O_4H_{26}$

The compound crystallizes in the monoclinic system, space group $P2_1$, with the unit cell parameters a = 11.281(5), b = 13.151(5), c = 13.715(5) Å, β = 110.890(5) ° i Z = 2, ρ_x = 1.210 g cm^{-3}, μ = 0.085 mm^{-1}. The final R factor is 0.046 for 4481 independent reflections and 483 parameters.

Authors would like to thank the Provincial Secretariat for Science and Technological Development for financial support (Project No. 114-451-1987/2011-01).

[1] CrysAlisPro Software system; Oxford Diffraction Ltd., vers. 171.32 Oxford, UK, 2007.
[2] Altomare et al. J. Appl. Cryst. 1999, 32, 115-119.
[3] Sheldrick, G. M. (1997). SHELX97. University of Göttingen, Germany

SINTEZA I KRISTALNA STRUKTURA 3E,6E-DIHIDROKSIMINO-17-OKSA-D-HOMOANDROST-4-EN-16-ONA

M. Savić [a], O. Klisurić [b], J. Ajduković [a], A. Oklješa [a], A. Gaković [a], E. Djurendić [a], S. Jovanović-Šanta [a], K. Penov Gaši [a]

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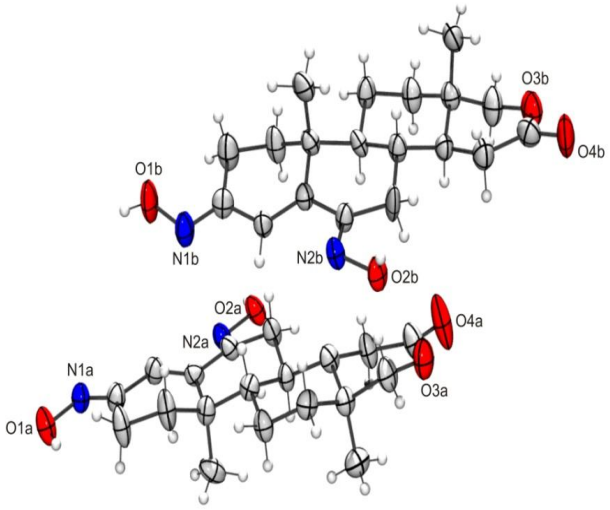
Višefaznom sintezom iz dehidroepiandrosterona dobijeno je novo jedinjenje 3E,6E-dihidroksimino-17-oksa-D-homoandrost-4-en-16-on sa potencijalnom biološkom aktivnošću. Struktura novosintetizovanog jedinjenja je potvrđena na osnovu spektroskopskih podataka (IR, ^{1}H-NMR, ^{13}C-NMR), kao i rendgenskom strukturnom analizom.



Slika 1. Prikaz molekulske strukture $C_{19}N_2O_4H_{26}$

Kristalografski podaci za novosintetisano jedinjenje su dobijeni na sobnoj temperaturi na Oxford Diffraction Gemini S difraktometru uz upotrebu Mo Kα zračenja (λ = 0,7107 Å). Programski paket CrysAlis^{Pro} [1] upotrebljen je za prikupljanje, semi-empirijsku korekciju na apsorpciju i redukciju podataka. Struktura je rešena uz pomoć direktnih metoda upotrebom SIR97 [2] programa i utačnjena upotrebom SHELXL-97 programa [3].

Jedinjenje kristališe u monokliničnom kristalografskom sistemu, prostorna grupa $P2_1$, sa parametrima elementarne ćelije: a = 11,281(5), b = 13,151(5), c = 13,715(5) Å, β = 110,890(5) ° i Z = 2, ρ_x = 1,210 g cm^{-3}, μ = 0,085 mm^{-1}. Konačna vrednost R faktora je 0,046 za 4481 nezavisnih refleksija i 483 parametara.

[1] CrysAlisPro Software system; Oxford Diffraction Ltd., vers. 171.32 Oxford, UK, 2007.
[2] Altomare et al. J. Appl. Cryst. 1999, 32, 115-119.
[3] Sheldrick, G. M. (1997). SHELX97. University of Göttingen, Germany

X-RAY STRUCTURAL ANALYSIS OF NEWLY SYNTHESIZED STEROIDAL SALICYLOYL DERIVATIVE

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In order to study the influence of the 3-substituted 17β-salicyloyl derivative on antioxidant activity, 3-methoxyestra-1,3,5(10)-trien-17β-yl salicylate was synthesized starting from 3-methoxy estradiol. Newly steroidal salicyloyl derivative was prepared by conventional heating of a mixture consisting of methyl salicylate and the corresponding steroidal compound and metallic sodium as a catalyst.

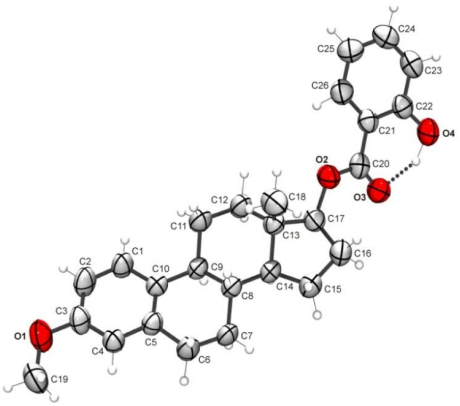

Figure 1. A view of molecular structure of $C_{26}O_4H_{30}$

X-ray structure analysis and molecular mechanics calculations (MMC) were performed for compound to define the conformation in terms of energy minima. A comparison of crystal and MMC structure revealed that intramolecular hydrogen bonding plays an important role in stabilizing molecular conformation.

The compound crystallizes in the monoclinic system, space group $P2_1$, with the unit cell parameters, a = 8.7603(5), b = 7.3556(4), c = 16.8503(9) Å, β = 90.743(5) ° and Z = 2, ρ_x = 1.244 g cm^{-3}, μ = 0.08 mm^{-1}. The final R factor is 0.032 for 2312 independent reflections and 369 parameters.

Authors would like to thank the Hungary-Serbia IPA Cross-border Co-operation Programme (Project No. HUSRB/1002/214/133)

STRUKTURNA ANALIZA NOVOSINTETIZOVANOG STEROIDNOG SALICILOIL DERIVATA

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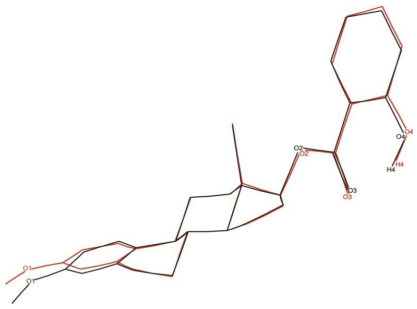
U cilju ispitivanja uticaja 3-supstituisanih 17β-saliciloil derivata na antioksidantnu aktivnost, 3-metoksiestra-1,3,5(10)-trien-17β-il salicilat je sintetisan polazeći od 3-metoksi estradiola. Novi steroidni saliciloil derivat je dobijen konvencionalnim zagrevanjem smeše metil salicilata, odgovarajućeg steroidnog jedinjenja i metalnog natrijuma kao katalizatora. Molekulska struktura ispitivanog jedinjenja je podvrgnuta molekularno mehaničkim proračunima (MMC) radi određivanja konformacije molekula u energetskom minimumu. Komparacija kristalne i MMC strukture je pokazala da intramolekularne vodonične veze igraju značajnu ulogu u stabilizaciji molekulske konformacije.



Slika 1. Superponirane kristalna i MMC struktura molekula $C_{26}O_4H_{30}$

Jedinjenje kristališe u monokliničnom kristalografskom sistemu, prostorna grupa $P2_1$, sa parametrima elementarne ćelije: a = 8,7603(5), b = 7,3556(4), c = 16,8503(9) Å, β = 90,743(5) ° i Z = 2, ρ_x = 1,244 g cm^{-3}, μ = 0,08 mm^{-1}. Konačna vrednost R faktora je 0,032 za 2312 nezavisnih refleksija i 369 parametara.

BETTER DATA – PROPER REDUNDANCY.

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It has been demonstrated repeatedly that high redundancy is a very desirable data set characteristic, leading to reduced statistical errors and ultimately more precise intensity information (see, for example [1]). Consequently, average redundancy is a figure which is usually supplied when diffraction data is reported. However, when symmetry is high and unit cells are small, which applies for many solid state compounds, this average number is misleading for reflections with a low number of symmetry equivalents. Good examples are P4/mmm or P6/mmm, where a general reflection *hkl* has 16 or 24 equivalents, while *00l*-reflections only comprise two. In a data set with a certain average redundancy, there exists a fair chance that general reflections have been, as a consequence of these symmetry conditions, observed many times more often than the axial reflections, severely skewing the redundancy distribution and pushing the average redundancy to a higher value. Furthermore, the intensity information of these axial reflections is based on very few values only and therefore less reliable.

In order to achieve high redundancy for *each* reflection, not just the general ones, we developed a data collection strategy software which provides the possibility to take care of those „symmetry impaired“ reflections. The resulting software turned out to be rather flexible, providing the ability to use a very wide range of indicators beyond redundancy for strategy determination. It is hardware independent and can easily be configured for use with different goniometers and detectors. Beyond strategy calculation it also contains tools for detailed analysis of measured diffraction data sets.

[1] Vogel Jørgensen, M. R., Svendsen, H., Stokkebro Schmøkel, M., Overgaard, J. & Iversen, B. B., (2012). Acta Crystallogr., A**68**, 301-303.

MECHANICAL ACTIVATION AND SYNTHESIS OF SPHENE BASED CERAMIC MATERIAL

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Sphene ($CaTiSiO_5$), a major crystalline phase in a calcium titanosilicate ceramic material has been prepared from a powder mixture of stoichiometric amounts of $CaCO_3$, TiO_2 and SiO_2 using vibro-milling for homogenization and activation of precursors. The mechanochemical process initially yielded amorphous powders, which on further calcination, crystallized to yield sphene ceramic. Before any calcinations, the average particle size and particle size distribution were determined by particle size analyzer. All of the powders were characterized at room temperature by X-ray powder diffraction. Powder morphology and particle size distribution were analyzed by scanning electron microscopy and laser diffraction, respectively. Determination of the melting point of sintered sphene was followed by hot-stage microscopy. Rietveld refinement (Fig. 1) was employed to get the structural information of the synthesized powder. The most favorable conditions for mechanical activation and synthesis of sphene based ceramic material are reported.
Keywords: Sphene; Mechanochemistry; Rietveld refinement; SEM/EDS

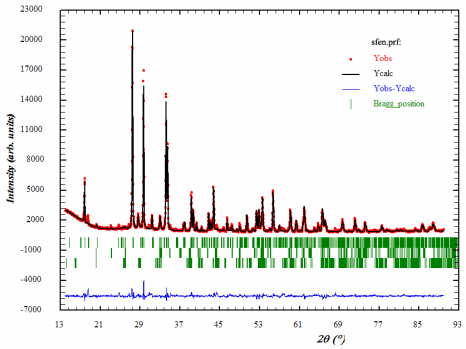

Fig.1. Rietveld refinement plot of the X-ray powder diffraction data of the sphene heated at 1200 °C. In the figure the continuous line represents the calculated pattern, while circles show the observed pattern. The residual curve is plotted below. Vertical bars represent reflection positions: first row sphene, second row perovskite and third row coesite.

МЕХАНОХЕМИЈСКА АКТИВАЦИЈА И СИНТЕЗА КЕРАМИЧКОГ МАТЕРИЈАЛА НА БАЗИ СФЕНА

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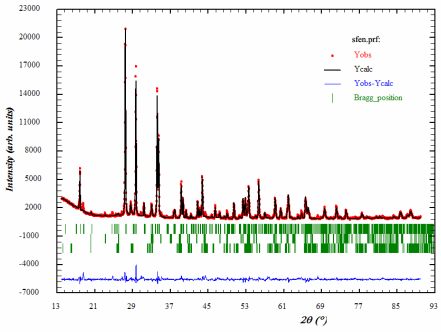
Сфен ($CaTiSiO_5$), као већинска фаза керамичког материјала на бази калцијум титаносиликата је припремљен од стехиометријске мешавине прахова $CaCO_3$, TiO_2 и SiO_2 користећи вибро-млин за хомогенизацију и активацију прекурсора. Механохемијски процес је првобитно дао аморфне прахове, који даљом калцинацијом кристалишу дајући керамику на бази сфена. Пре било какве калцинације, просечна величина честица и дистрибуција су одређене методом PSA. Сви прахови су окарактерисани методом рендгенске дифракције праха. Морфологија и расподела величина честица су анализирани методом скенирајуће електронске микроскопије као и методом ласерске дифракције. Тачка топљења синтерованог сфена одређена је методом термо микроскопа. Ритвелдовом методом (сл. 1) утачњена је структура синтетизованог праха. У раду су приказани најповољнији услови за механохемијску активацију и синтезу керамичког материјала на бази сфена.
Кључне речи: Сфен; Механохемија; Ритвелдова метода; SEM/EDS



Слика 1. Дифрактограм праха сфена жареног на температури од 1200 °C. На слици континуална линија представља утачњавани, док кругови представљају експериментално добијени структрурни модел. Резидуална крива је нацртана испод. Вертикалне линије представљају следеће рефлексије: први ред припада рефлексијама сфена, други перовскита и трећи ред коесита.

CRYSTAL STRUCTURE OF 4-HYDROXY-3-(1-(*p*-TOLYLIMINO)ETHYL)-2*H*-CHROMEN-2--ONE-PALLADIUM(II) COMPLEX

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Complex 4-hydroxy-3-(1-(*p*-tolylimino)ethyl)-2*H*-chromen-2-one-palladium(II) was obtained by direct reaction of potassium-tetrachloridopalladate(II) and 4-hydroxy-3--(1-(*p*-tolylimino)ethyl)-2*H*-chromen-2-one in molar ratio 1:2. The mixture was heated on 50 °C and stirred for 2 h. The complex 4-hydroxy-3-(1-(*p*-tolylimino)ethyl)-2*H*-chromen-2--one-palladium(II) as a yellow precipitate was filtered, washed with water and air-dried. Suitable crystal for X-ray analysis was obtained by recrystallization from chloroform.

Crystallographic data: crystal system-triclinic, space group *P*-1, crystal size 0.35 × 0.26 × 0.21 mm, a = 10.022(5), b = 10.534(5), c = 10.735(5) Å, α = 111.224(5), β = 110.920(5), γ = 94.812(5) °, V = 956.8(8) Å^3 and Z = 1, ρ_x = 1.614 g cm^{-3}, μ = 0.953 mm^{-1}. The refinement on F^2 (279 parameters and 3358 independent reflections) yielded R [$F^2 > 2\sigma(F^2)$] = 0.045, $wR(F^2)$ = 0.095, S = 1.03.

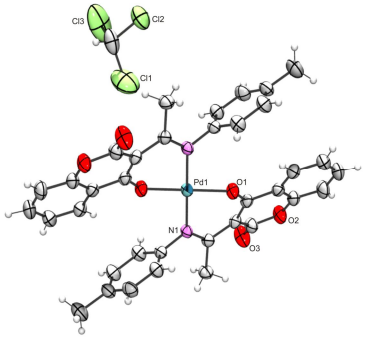

Figure 1. ORTEP plot for 4-hydroxy-3-(1-(*p*-tolylimino)ethyl)-2*H*-chromen-2--one-palladium(II) complex

KRISTALNA STRUKTURA 4-HIDROKSI-3-(1-(*p*-TOLILIMINO)ETIL)-2*H*-HROMEN-2-ON-PALADIJUM(II) KOMPLEKSA

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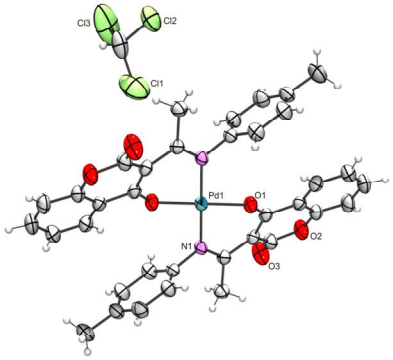
Kompleks 4-hidroksi-3-(1-(*p*-tolilimino)etil)-2*H*-hromen-2-on-paladijum(II) je dobijen direktnom reakcijom između kalijum-tetrahloridopaladata(II) i 4-hidroksi-3-(1-(*p*-tolilimino)etil)-2*H*-hromen-2-on liganda u molskom odnosu 1:2. Reakciona smeša je zagrevana na 50 °C uz mešanje. Žuti talog 4-hidroksi-3-(1-(*p*-tolilimino)etil)-2*H*-hromen-2-on-paladijum(II) kompleksa je odvojen ceđenjem, ispran destilovanom vodom i sušen na vazduhu. Odgovarajući kristali pogodni za rendgensku strukturnu analizu dobijeni su prekristalizacijom iz hloroforma.

Kristalografski podaci: kristalni sistem-triklinični, prostorna grupa *P*-1, veličina kristala 0,35 × 0,26 × 0,21 mm, a = 10,022(5), b = 10,534(5), c = 10,735(5) Å, α = 111,224(5), β = 110,920(5), γ = 94,812(5) °, V = 956,8(8) Å^3 i Z = 1, ρ_x = 1,614 g cm^{-3}, μ = 0,953 mm^{-1}. Utačnjavanje sa F^2 (279 parametara i 3358 nezavisnih refleksija) dalo je R [$F^2 > 2\sigma(F^2)$] = 0,045, $wR(F^2)$ = 0,095, S = 1,03.



Slika 1. Struktura 4-hidroksi-3-(1-(*p*-tolilimino)etil)-2*H*-hromen-2-on-paladijum(II) kompleksa

CRYSTAL STRUCTURE OF $[Cu_2L_2(H_2O)_2](SO_4)_2 \cdot 2H_2O$ (L = PYRIDOXAL THIOSEMICARBAZONE)

Marko V. Rodić, Vukadin M. Leovac, Ljiljana S. Vojinović-Ješić, Vladimir Divjaković

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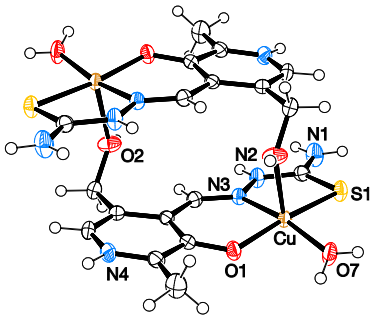
Dark green single crystals of the title complex were prepared by the reaction of slightly acidic (H_2SO_4) methanol solutions of $CuSO_4 \cdot 5H_2O$ and pyridoxal thiosemicarbazone (L) in mole ratio 1:1. Dinuclear complex cation has centrosymmetric structure. The Cu(II) is situated in a square-pyramidal environment ($\tau = 0.04$). The equatorial plane is formed by ligators of ONS coordinated L and one water molecule, while the apical position is occupied by hydroxymethyl oxygen $O(2)^i$ (i = $-x$, $1-y$, $-z$) of the bridging ligand. The Cu atom is shifted towards the apical oxygen atom by 0.173(12) Å. The Cu–atom ligator bond lengths are in the range 1.917(2)–1.967(2) Å for O(1) N(3) and O(7), while Cu–S(1) and $Cu–O(2)^i$ are longer (2.2998(9) Å and 2.233(2) Å, respectively). Pyridoxal thiosemicarbazone is coordinated in neutral, zwitterionic form as tetradentate bridging ligand, *i.e. via* phenol oxygen, hydrazine nitrogen, sulfur and hydroxymethyl oxygen, which, as the bridging ligator, connects the subunits. Such coordination results in formation of two metallocycles, five-membered (thiosemicarbazide) and six-membered (pyridoxilidene). The coordinated ligand slightly deviates from planarity, and dihedral angles between pyridine ring, six- and five-membered metallocycles are 7.54(10)°, 4.80(7)°, respectively. The six-membered metallocycle is in screw-boat conformation and is described by the following puckering parameters: Q = 0.200(2) Å, θ = 67.9(9)°, φ = 34.3(9)°, while the other rings are planar. Crystal structure of the complex is stabilized by an extended inter- and intra-molecular 3D hydrogen-bond network. It can be mentioned that all possible hydrogen donors are involved in hydrogen-bonding, and that sulfate anion acts as multiple hydrogen acceptor.



The data were collected on Gemini S diffractometer (Agilent Technologies) using MoKα radiation (λ = 0.71069 Å), and were corrected for Lorentz, polarization and background effects. The structure was solved by direct methods using SIR92 and refined by full matrix least square methods on F^2 using SHELXL-97 to R = 0.036. *Crystallographic data:* $C_{18}H_{32}Cu_2N_8O_{16}S_4$, M_r = 871.90, monoclinic, space group $P2_1/n$, a = 7.2529(2) Å, b = 11.1766(4) Å, c = 18.8522(6) Å, β = 93.751(3)°, V = 1524.94(8) Å^3, Z = 2, μ(MoKα) = 1.756 mm^{-1}, S = 1.059.

KRISTALNA STRUKTURA $[Cu_2L_2(H_2O)_2](SO_4)_2{\cdot}2H_2O$ (L = TIOSEMIKARBAZON PIRIDOKSALA)

Marko V. Rodić, Vukadin M. Leovac, Ljiljana S. Vojinović-Ješić, Vladimir Divjaković

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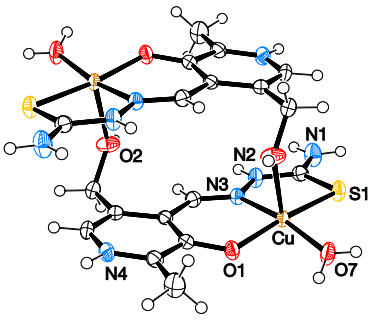
Tamno zeleni kristali naslovljenog kompleksa su dobijeni reakcijom blago zakišeljenih (H_2SO_4) metanolnih rastvora $CuSO_4{\cdot}5H_2O$ i tiosemikarbazona piridoksala (L) u molskom odnosu 1:1. Dinuklearni kompleksni katjon ima centrosimetričnu strukturu. Cu(II) se nalazi u kvadratno-piramidalnom okruženju (τ = 0,04) čiju ekvatorijalnu ravan formiraju ligatori ONS koordinovanog L i molekul vode, dok se u apikalnom položaju nalazi atom kiseonika hidroksimetil grupe $O(2)^i$ (i = $-x$, $1-y$, $-z$) susednog molekula liganda, koji ima mostovnu ulogu. Atom Cu odstupa od bazalne ravni i pomeren je za 0,173(12) Å ka apikalnom atomu kiseonika. Dužine veza Cu–atom ligator su u opsegu 1,917(2)–1,967(2) Å za O(1), N(3) i O(7), dok su veze Cu–S(1) i Cu–$O(2)^i$ duže (2,2998(9) i 2,233(2) Å, respektivno). Tiosemikarbazon piridoksala je koordinovan u neutralnoj, cviterjonskoj formi, kao tetradentatni mostovni ligand, tj. preko fenolnog atoma kiseonika, hidrazinskog atoma azota, atoma sumpora i atoma kiseonika hidroksimetil grupe, koji kao mostovni ligator povezuje subjedinice. Na taj način nastaju dva metalocikla, petočlani (tiosemikarbazidni) i šestočlani (piridoksilidenski). Koordinovani ligand blago odstupa od planarnosti, pri čemu su diedralni uglovi između piridinskog prstena, šestočlanog i petočlanog metalocikla 7,54(10)° i 4,80(7)°, respektivno. Šestočlani metalocikl se nalazi u konformaciji „uvijene lađe“ i opisan je sledećim parametrima nabiranja: Q = 0,200(2) Å, θ = 67,9(9)°, φ = 34,3(9)°, dok su ostali prstenovi planarni. Kristalna struktura kompleksa je stabilizovana razgranatom 3D mrežom inter- i intra-molekulskih vodoničnih veza. Važno je napomenuti da svi potencijalni vodonik-donori učestvuju u građenju vodoničnih veza, pri čemu je sulfatni anjon višestruki vodonik akceptor.



Difrakcioni podaci su prikupljeni na Gemini S difraktometru (Agilent Technologies) korišćenjem MoKα zračenja (λ = 0,71069 Å). Izvršena je korekcija na Lorencov, polarizacioni i efekat pozadinskog šuma. Struktura je rešena direktnom metodom pomoću programa SIR92 i utačnjena metodom najmanjih kvadrata pomoću programa SHELXL-97 do R = 0,036. *Kristalografski podaci:* $C_{18}H_{32}Cu_2N_8O_{16}S_4$, M_r = 871,90, monoklinični sistem, prostorna grupa $P\,2_1/n$, a = 7,2529(2) Å, b = 11,1766(4) Å, c = 18,8522(6) Å, β = 93,751(3)°, V = 1524,94(8) $Å^3$, Z = 2, μ(MoKα) = 1,756 mm^{-1}, S = 1,059.

POLYMERIC MANGANESE(II) COMPLEX WITH ISOPHTHALATE IONS AND 2,2'-DIPYRIDYLAMINE

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In the past decade the design and synthesis of metal-organic coordination polymers with anions of isophthalic (H_2ipht, 1,3-benzenedicarboxylic) acid have become a growing field in crystal engineering due to their structural diversity and potential application as functional materials [1]. We have been continually interested in synthesis and characterisation of ternary transition metal complexes containing polycarboxylate anions and some aromatic N,N'-donor ligands [2,3]. As a continuation of our research, the polymeric complex, $[Mn(dipya)(ipht)]_n$, where dipya is 2,2'-dipyridylamine, represents a novel example.

In hydrothermally synthesized $[Mn(dipya)(ipht)]_n$, ipht anion bridges three Mn atoms with bidentate-bridging and monodentate COO groups. In this way centrosymmetric double chains extending along *c*-axis are formed (Figure). Mn(II) ions are in a deformed square pyramidal environment consisting of two N atoms from chelating dipya ligand and three O atoms from three different ipht ligands. Two crystallographically different Mn(II) ions are linked by two bridging ipht ligands to construct eight-membered $[Mn_2O_4C_2]$ rings. Similar rings are already found in the ipht structures where at least one bidentate-bridging COO group exist [3].

Double chains are stacked by face to face π-π interactions at centroid-centroid distances of 3.67 and 3.79 Å. Uncoordinated O atoms from monodentate COO groups and the amine H atoms of dipya build hydrogen bonds, which connect adjacent chains. Therefore, through π-π interactions and hydrogen bonds the chains are packed into a three-dimensional framework.

Crystal data: $C_{18}H_{13}MnN_3O_4$, $M_r = 390.25$, monoclinic, space group *C*2/*c*, $a = 14.8320(6)$, $b = 21.9325(6)$, $c = 11.9995(5)$ Å, $\beta = 122.916(6)$ °, $V = 3276.8(2)$ Å^3, $Z = 8$, $F(000) = 1592$, $\rho_x = 1.582$ g cm^{-3}, μ(Mo Kα) = 0.836 mm^{-1}. The refinement on F^2 (287 parameters) yielded $R_1 = 0.037$, $wR_2 = 0.067$, $S = 0.97$ for all data, and $R_1 = 0.027$ for 2478 observed reflections with $I \geq 2\sigma(I)$.

[1] F. P. Huang, J. L. Tian, G. J. Chen, D. D. Li, W. Gu, X. Liu, S. P. Yan, D. Z. Liao, P. Cheng, Cryst. Eng. Comm., 12 (2010), 1269-1279.

[2] J. Rogan, D. Poleti, Lj. Karanović, Acta Crystallogr., C67 (2011), m230-m233.

[3] J. Rogan, D. Poleti, Lj. Karanović, Z. Jagličić, J. Mol. Struct., 985 (2011), 371-379.

POLIMERNI MANGAN(II)-KOMPLEKS SA IZOFTALAT-JONIMA I 2,2'-DIPIRIDILAMINOM

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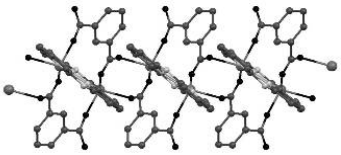
Zbog strukturne različitosti metal-organskih koordinacionih polimera sa anjonima izoftalne (H_2ipht, 1,3-benzendikarboksilne) kiseline i njihove potencijalne primene kao funkcionalnih materijala, tokom prošle decenije dizajn i sinteza ovih jedinjenja predstavljaju stalno rastuće polje istraživanja u kristalnom inženjerstvu [1]. Mi se kontinualno bavimo sintezom i karakterizacijom ternernih kompleksa prelaznih metala koji sadrže aromatične polikarboksilat-jone i neke N,N'-donorske ligande [2,3]. Polimerni kompleks $[Mn(dipya)(ipht)]_n$, gde je dipya = 2,2'-dipiridilamin, predstavlja novi primer takvih jedinjenja.

Kod hidrotermalno dobijenog $[Mn(dipya)(ipht)]_n$ kompleksa, ipht-anjon premošćava tri atoma Mn preko bidentatno-mostovnih i monodentatnih COO^--grupa. Na taj način nastaju centrosimetrični dvostruki lanci koji se protežu duž *c*-ose (slika). Mn(II)-joni su u deformisanom kvadratno-piramidalnom okruženju koje čine dva atoma N iz helatnog dipya liganda i tri atoma O iz tri različita ipht liganda. Dva kristalografski različita Mn(II)-jona povezana su preko dva mostovna ipht liganda tako da grade osmočlane $[Mn_2O_4C_2]$ prstenove. Slični prstenovi već su nađeni kod ipht-struktura gde postoji najmanje jedna bidentatno-mostovna COO^--grupa [3].

Dvostruki lanci povezani su „face-to-face" π-π interakcijama sa centroid-centroid rastojanjima od 3,67 i 3,79 Å. Nekoordinirani atomi O iz monodentatnih COO^--grupa i aminski atomi H iz dipya grade vodonične veze koje povezuju susedne lance. Tako se lanci preko π-π interakcija i vodoničnih veza pakuju u trodimenzionalnu mrežu.



Kristalografski podaci: $C_{18}H_{13}MnN_3O_4$, M_r = 390,25, monoklinični sistem, prostorna grupa *C*2/*c*, a = 14,8320(6), b = 21,9325(6), c = 11,9995(5) Å, β = 122,916(6) °, V = 3276,8(2) Å^3, Z = 8, $F(000)$ = 1592, ρ_x = 1,582 g cm^{-3}, μ(Mo Kα) = 0,836 mm^{-1}. Utačnjavanje sa F^2 (287 parametara) dalo je R_1 = 0,037, wR_2 = 0,067, S = 0,97 za sve podatke, i R_1 = 0,027 za 2478 refleksija sa $I \geq 2\sigma(I)$.

[1] F. P. Huang, J. L. Tian, G. J. Chen, D. D. Li, W. Gu, X. Liu, S. P. Yan, D. Z. Liao, P. Cheng, Cryst. Eng. Comm., 12 (2010), 1269-1279.

[2] J. Rogan, D. Poleti, Lj. Karanović, Acta Crystallogr., C67 (2011), m230-m233.

[3] J. Rogan, D. Poleti, Lj. Karanović, Z. Jagličić, J. Mol. Struct., 985 (2011), 371-379.

ELECTRON DENSITY STUDY OF A *SYN*-FACIAL Cr-Mn COMPLEX. TOWARD THE UNDERSTANDING OF THE SUBTILITY OF A HETEROMETALIC BOND

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A few years ago, a peculiar class of air-stable electron-deficient *syn*-facial heterobimetallic compounds, accounted for as *syn*-facial Cr,Mn benzyl complexes, were synthesized by the sequential reaction of organolithium reagents and methyltriflate with cyclomanganated (η6-arene)$Cr(CO)_3$ complexes [1]. Three limiting forms (A, B and C) are used to describe *syn*-facial heterobimetallic Cr, Mn benzyl complexes. Each form entails different consequences over the bonding modes of the organic ligand, oxidation state of the metals and over molecular geometry. Form A implies i) a significant shortening of the C_{Ar}–C_{benzyl} as a result of its increased ethylenic character, ii) a significant shortening of the Mn-to-C_{benzyl} bond, and iii) a pronounced folding of the Cr-bound arene ligand due to pentahapticity. In both limiting forms B and C, the Mn center binds the benzylic position through a σ-bond and the η6 bonding mode of the Cr-bound arene ligand is preserved.
We have performed two low temperature single crystal X-ray diffraction experiments on *syn*-facial Cr,Mn benzyl complex at synchrotron Soleil. Despite the difficulties encountered during the data reduction and the methanol disordered solvent, we have finally been able to determine the electron and electrostatic properties of the compound. The results will be discussed in order to better understand the subtility of the heterometalic bond.

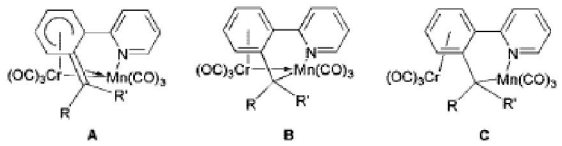

Figure: The three formulations for the title benzylic complex as proposed originally according to the general covalent bond formalism.

[1] a) J.P. Djukic, et al Eur. J. Inorg. Chem. (1998), 1781-1790 b) J.P. Djukic, et al Organometallics 19 (2000), 5484-5499 c) C. Michon, et al Organometallics 21 (2002), 3519-335 d) J.P. Djukic,et al J. Organomet. Chem., 2006, 691, 846-858

ISPITIVANJE ELEKTRONSKE GUSTINE U *SYN*-FACIJALNOM Cr-Mn KOMPLEKSU SA CILJEM BOLJEG RAZUMEVANJA HETEROMETALNIH VEZA

Sladjana Novaković[1,3], Shi Xiaoxuan[1], Anne Spasojević-de Biré[1*], Pierre Fertey[2], Nicolas Guiblin[1], Carlo Gatti[4], Jean-Pierre Djukić[5]

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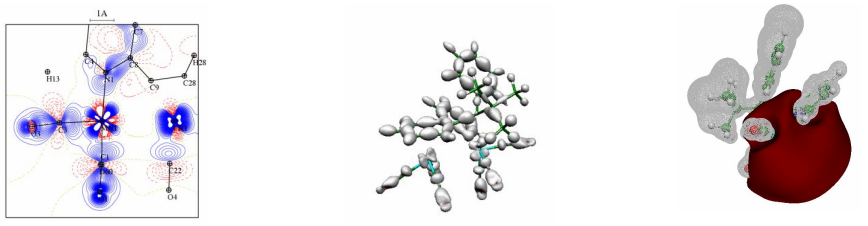
Pre nekoliko godina, neobična klasa elektron–deficitarnih *syn*-facijalnih, heterobimetalnih kompleksa stabilnih na vazduhu, sintetisana je reakcijom organolitijumovih reagenasa i metiltriflata sa ciklomanganatnim (η6-aren)$Cr(CO)_3$ kompleksima [1]. Novonastali, *tzv*. *syn*-facijalni Cr,Mn benzil kompleksi, predstavljeni su kroz tri granične forme. Svaka od formi podrazumeva različit način vezivanja organskog liganda, različito oksidaciono stanje metala, kao i različitu geometriju molekula. Forma A podraumeva: i) značajno skraćenje C_{Ar}–C_{benzil} veze kao rezultat povećanja dvostrukog karaktera, ii) značajno skraćenje rastojanja između atoma Mn i C_{benzil} i (iii) naglašenu deformacija arena vezanog za atom Cr usled pentaheptatnosti. U formama B i C, Mn se vezuje za benzilni fragment posredstvom σ-veze, dok je heksaheptatnost arna u odnosu na Cr sačuvana. Na sihrotronu Soleil izveli smo dva niskotemperaturna eksperimenta difrakcije rendgenskog zračenja sa monokristala *syn*-facijalnog Cr,Mn benzil kompleksa. Pored teškoća koje su se javile u toku redukcije podataka i usled prisustva neuređenog molekula metanola uspeli smo da odredimo elektronska i elektrostatička svojstva ovog jedinjenja. Cilj rezultata koji će biti prezentovani je bolje razumevanje veza koje se ostvaruju između atoma različitih metala .



a b c

Slika a) 2-D statička deformaciona elektronska gustina, b) 3-D statička deformaciona elektronska gustina, c) 3-D izopovršine elektrostatičkog potencijala

[1] a) J.P. Djukic, et al Eur. J. Inorg. Chem. (1998), 1781-1790 b) J.P. Djukic, et al Organometallics 19 (2000), 5484-5499 c) C. Michon, et al Organometallics 21 (2002), 3519-335 d) J.P. Djukic,et al J. Organomet. Chem., 2006, 691, 846-858

HIGH RESOLUTION X-RAY DIFFRACTION, *AB INITIO* CALCULATIONS AND THERMODYNAMIC MEASUREMENTS TO GAIN INSIGHT ON THE POLYMORPHISM OF DRUGS. APPLICATION TO PIRACETAM

Nouha El Hassan[a], Anne Spasojević – de Biré[a], Jean-Michel Gillet[a], Nour-Eddine Ghermani[a,b], Philippe Espeau[c], Yohan Corvis[c], Camille Alzina[c]

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Studying the polymorphism of pharmaceutical compounds is a growing field of activity. This is due, on one hand, to the economic pressure of the pharmaceutical industry, and on the other hand, to the more important awareness of the consequences of polymorphism on the properties of a medicine.
A good knowledge of molecular interactions and crystal energies is essential for the determination of relative polymorph stability. We have developed a fundamental approach to study polymorphism, which combines high-resolution X-ray diffraction and *ab- initio* calculations. This approach would enable us to study the consequences of drug polymorphism on the physical and chemical properties of drugs.
Piracetam is a small and flexible molecule, used against several neurodegenerative disorders such as Alzheimer's disease. We will present the results we have obtained for Piracetam (Figure). In particular, we will compare electrostatic energies obtained from X ray diffraction experiments [1] with crystal structure prediction from ab-initio calculations [2]. We will show also thermodynamic aspect of the relative stability for piracetam.

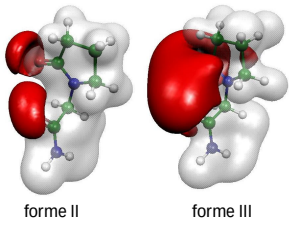


Figure. Experimental electrostatic potential isosurface (red -0.1 e.Å-1 grey +0.1 e.Å-1) for piracetam polymorphs I and II

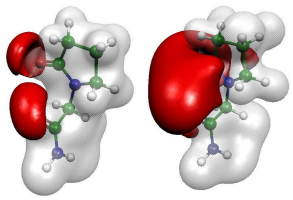
[1] Chambrier, M.-H. ; Bouhmaida, N.; Bonhomme, F.; Lebègue, S.; Gillet J.-M., Jelsch, C. and Ghermani N.E. ; Cryst. Growth Des., 2011, 11,6, 2528-2538
[2] Nowell, H. and Price S.L., Acta Cryst., 2005, B61, 558–568

RENDGENSKA DIFRAKCIJA VISOKE REZOLUCIJE, *AB INITIO* IZRAČUNAVANJA I TERMODINAMIČKA MERENJA U ISPITIVANJU POLIMORFIZMA KOD LEKOVA. PRIMENA NA PRIACETAMU

Nouha El Hassan[a], Anne Spasojević – de Biré[a], Jean-Michel Gillet[a], Nour-Eddine Ghermani[a,b], Philippe Espeau[c], Yohan Corvis[c], Camille Alzina[c]

[a]Laboratoire Structures et Propriétés des Matériaux Solides (SPMS), UMR CNRS 8580, Ecole Centrale Paris, Grande Voie des Vignes, 92290 Châtenay-Malabry, Francuska; [b] Laboratoire Physico-Chimie-Pharmacotechnie-Biopharmacie (PPB), UMR CNRS 8612, Université Paris-Sud 11, Faculté de Pharmacie, 5 rue Jean- Baptiste Clément, 92296 Châtenay-Malabry, Francuska; [c] Laboratoire de chimie physique, Faculté de Pharmacie de I'Université Paris 5, 4 avenue de I'Observatoire, 75006 Paris, Francuska
e-mail: anne.spasojevic@ecp.fr

Ispitivanje polimorfizma kod jedinjenja koja se koriste u faramciji je u porastu. Razlog je svakako ekonomski pritisak na faramceutsku industriju, ali takodje i svest o posledicama koje polimorfizam može imati na svojstava medikamenata.
Poznavanje molekulskih interakcija i energije kristala je od suštinskog značaja za određivanje relativne stabilnosti polimorfa. Razvili smo fundamentalni pristup u proučavanjau polimorfizma koji kombinuje rendgensku strukturnu analizu visoke rezolucije i *ab initio* metode. Ovakav pristup omogućiće proučavanje polimorfizma kod lekovam kao i posledica koje polimorfizam može imati na njihova fizička i hemijska svojstva.
Piracetam je mali i fleksibilni molekul koji se koristi protiv nekoliko neurodegenrativnih poremećaja kao što je Alchajmerova bolest. Ovom prilikom izložićemo rezultate koje smo dobili za Priacetam (Slika) poredeći, pre svega, elektrostatičke energije dobijene eksperimentima rendgenske difrakcije [1] sa kristalnom strukturom predviđenom *ab initio* izračunavanjima [2]. Pokazaćemo takođe, termodinamičke aspekte relativne stabilnosti piracetama.



Slika. Eksperimentalno određeni elektrostatički potencijal za polimorfe piracetama I i II (izopovršine: crvena -0.1 e.Å-1; siva +0.1 e.Å-1)

[1] Chambrier, M.-H.; Bouhmaida, N.; Bonhomme, F.; Lebègue, S.; Gillet J.-M., Jelsch, C. and Ghermani N.E.; Cryst. Growth Des., 2011, 11,6, 2528-2538
[2] Nowell, H. and Price S.L., Acta Cryst., 2005, B61, 558–568

COULD WE EASILY CHARACTERIZE THE CRYSTAL PACKING TYPE (DIMER, 1D, 2D, 3D)? APPLICATION TO SMALL ORGANIC MOLECULES

Aziza Ikni[a], Anaïs Mendre[a], Wenjing Li[a], Goran A. Bogdanović[b], Anne Spasojević-de Biré[a]

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[b]Vinča Institute of Nuclear Science, Laboratory of Theoretical Physics and Condensed Matter Physics, PO Box 522, 11001 Belgrade, Serbia

One explanation of the mechanism responsible for Non Photochemical Light Induced Nucleation (NPLIN) is based on the Kerr effect [1]. Clusters of different symmetries preexist in supersaturated solutions. On the one hand, clusters for which the polarizability tensor is rod-like will contribute to the crystallization of the polymorph of 1-D crystal packing under Linear Laser Polarization (LP). On the other hand, clusters for which the polarizability tensor is disk-like will contribute to the crystallization of the polymorph of 2-D crystal packing under Circular Laser Polarization (CP). In order to validate this hypothesis and to test the NPLIN method on compounds exhibiting polymorphs that could react differently to an LP or CP Laser, we would analyze the Cambridge Structural Database (CSD). Automatic characterization of the crystal packing type is still not straightforward. Some specific software examines inorganic compounds, [2] but for organic molecules this automatic examination still doesn't exist. The algorithm, currently in development, involves the following steps for extracting and sorting-out refcodes of polymorphs: i) Extraction of refcodes of potential polymorphs from CSD using the code source of CSD and excel tool (229855 refcodes) ii) Sorting the compounds according to the number of polymorphs per compound after elimination of multi-measurements (different sources or different temperatures) for the same polymorph (10346 refcodes) iii) Sorting these compounds by the number of existing polymorphs. In order to define and validate the criteria that could be used for automatic determination of the different crystal packing type (dimmer, 1D, 2D, 3D) we proceed as follows: i) Use of Mercury software for a manual determination of the crystal packing type of each refcode. ii) Exploit both the energy of each non-covalent interaction and the inter-atomic distance, as used in Mercury, for an automatic determination of the packing crystal type. The energy of non-covalent interactions is determined according to Espinosa curves [3] deduced from topology analysis of experimental high resolution study (Atom In Molecules method). iii) Carry-out a comparison, on some sample examples, with the assignation of experimented crystallographers.
After validation, this algorithm will be programmed and then could be incorporated in Mercury.

[1] Bruce A. Garetz *et al.* Physical review letters, (**2002**), 89,175501
[2] V.A. Blatov, Multipurpose crystallochemical analysis with the program package TOPOS, IUCr CompComm Newsletter, (**2006**), 7, 4-38
[3] E. Espinosa *et al.* Acta Cryst. (**1996**) B52, 519
[4] E. Espinosa *et al.* J. Chem. Phys., (**2002**) 117(12)

MOŽEMO LI JEDNOSTAVNO OKARAKTERISATI TIP KRISTALNE STRUKTURE (DIMER, 1D, 2D, 3D)? PRIMENA KOD MALIH ORGANSKIH MOLEKULA

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Jedno objašnjenje mehanizma, odgovornog za Non Photochemical Light Induced Nucleation (NPLIN), zasniva se na Kerr efektu [1]. Klasteri različitih simetrija već postoje u presićenim rastvorima. Grupe u kojima je tenzor polarizacije "rod-like" (štapićastog oblika) pod dejstvom linearne laser polarizacije (LP) doprinose kristalizaciji polimorfa sa preferentno jednodimenzionim kristalnim pakovanjem. Sa druge strane, grupe kod kojih je tenzor polarizacije "disk-like" (oblika diska) pod uticajem kružne laser polarizacije (CP) doprinose kristalizaciji polimorfa sa dvodimenzionalnim kristalnim pakovanjem. Da bi proverili ovu hipotezu i da bi testirali NPLIN na jedinjenjima koja daju polimorfe i koja bi mogla reagovati različito na LP i CP laser, analizirali smo Kembričku banku kristalografskih podataka (Cambridge Structural Database, CSD). Automatska karakterizacija tipa kristalne strukture još uvek nije jednostavna. Za sada postoje kompjuterski programi za automatsko proučavanje neorganskih jedinjenja [2], ali ne i za organska jedinjenja. Algoritam koji se trenutno razvija se sastoji iz sledećih koraka za dobijanje i sortiranje referentnih kodova polimorfa:

- Ekstrakcija referentnih kodova mogućih polimorfnih struktura iz CSD baze, koristeći CSD kod i excel (229855 referentnih kodova).
- Sortiranje jedinjenja na osnovu broja polimorfa po jedinjenju nakon eliminacije struktura istog polimorfa (10346 referentnih kodova) koje su određene više puta (različiti izvor ili različite temperature).
- Sortiranje ovih jedinjenja na osnovu broja postojećih polimorfa.

Da bi definisali i proverili ovaj kriterijum, koji bi se mogao koristiti za automatsko odredjivanje tipa kristalne strukture (dimer, 1D, 2D, 3D), postupamo na sledeći način:

- Upotreba Mercury softvera za ručno odredjivanje tipa kristalne strukture za svaki referentni kod.
- Upotreba energije nekovalentne interakcije i medjuatomske udaljenosti, kao one korišćene u Mercury, za automatsko odredjivanje tipa kristalne strukture. Energija nekovalentne interakcije je odredjena na osnovu Espinosinih krivih [3] koje se dobijaju topološkom analizom nakon eksperimenta visoke rezolucije (Atom In Molecules method).
- Poredjenje rezultata o tipu kristalne strukture nekih uzoraka sa tipom kristalne strukture koje je eksperimentator odredio.

Nakon validacije, ovaj algoritam će biti kodiran u program koji će nakon toga biti uključen u Mercury.

[1] B. A. Garetz *et al.* Phys. Rev. Letters, (**2002**), 89, 175501. [2] V.A. Blatov, IUCr CompComm Newsletter, (**2006**), 7, 4-38. [3] E. Espinosa *et al.* Acta Cryst. (**1996**) B52, 519. [4] E. Espinosa *et al.* J. Chem. Phys., (**2002**) 117(12).

NPLIN OF GLYCINE AND CARBAMAZEPINE

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For decades, dramatic efforts have been made in order to understand nucleation processes using model molecules like glycine, the simplest amino acid. Glycine can be crystallized using different methods. One of them, NPLIN (Non Photochemical Light Induced Nucleation), allows selective crystallization of a polymorph in a particular range of supersaturation[1-8]. Recently, the capability of NPLIN to recrystallize the original structure through a memory effect has been established[7]. This selective crystallization (polymorph, or enantiomorph) would be of a great interest in the pharmaceutics industry.
Here we present a useful methodology for probing the feasibility of the NPLIN method. NPLIN is a laser induced crystallization method using a non-focused nanosecond laser beam at 532 nm or 1064 nm. Several compounds have been crystallized through NPLIN : urea[1], glycine[2], histidine[3], acetic acid[4], BPT[5], HEWL[5], KCl[6], $NaClO_3$[7], 5CB[8]. The main mechanism hypothesis is based on the non linear Kerr effect proposed by Garetz; that hypothesis is currently questioned[9].
One the one hand, the aim is the understanding of the nucleation mechanism involved in NPLIN through glycine and histidine, the only two molecules that have a selective crystallization depending on a particular LASER polarization (linear or circular). These experiments have been done at neutral pH; we are probing the switching effect at various pHs and under heavy water. Low and high pH[10] and heavy water[11] are well known to be favorable for γ polymorph.
On the other hand, we exposed carbamazepine to NPLIN. After exposing the supersaturated solutions to the laser we observed orange coloration, which is due to photochemical reaction. Moreover, after several hours, we observed crystallization in most of the tubes. We have for the first time shown that it is possible to obtain carbamazepine crystals using the NPLIN technique. We envisage to continue this experimental based study in order to determine the impact of a laser on the crystals morphology.

[1] Garetz et al. Phys. Rev. Lett. vol.77 (1996) n°16, [2] Zaccaro et al. Crystal Growth & Design vol.1 (2001) n°1, 5-8, [3] Sun et al. Crystal Growth & Design vol.8 (2008) n°5, 1720-1722, [4] Ward et al. Phys. Chem. Chem. Phys. Vol.14 (2012) 90 -93, [5] Lee et al. Crystal Growth & Design vol.8 (2008) n°12, 4255-4261, [6] Ward et al. Chemical Physics Letters 481 (2009) 25-28, [7] Ward et al. J. Chem. Phys. Vol. 135 (2011) 114508 [8] Sun et al., Phys. Rev. E vol.79 (2009) 021701, [9] Brandon et al. J. Chem. Phys. Vol. 134 (2011) 154501, [10] Lee et al. Crystal Growth & Design vol.8 (2008) n°1, 108-113 [11] Hughes et al. New J. Chem. Vol.33 (2009) 713–716.

NPLIN GLICINA I KARBAMAZEPINA

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Poslednje decenije, uloženi su veliki napori u cilju razumevanja procesa nukleacije koristeći model molekula kao što je jednostavna aminokiselina, glicin. Glicin možemo kristalisati koristeći različite metode. Jedna od njih NPLIN (Ne-Fotohemijska Svetlom Indukovana Nukleacija) dozvoljava selektivnu kristalizaciju polimorfa u posebnom opsegu presićenja[1-8]. Nedavno je pokazana sposobnost NPLINa da rekristališe originalnu strukturu kroz efekat pamćenja[7]. Ova selektivna kristalizacija (polimorf ili enantiomorf) bi bila od velikog interesa u farmaceutskoj industriji.

Ovde su predstavljene mogućnosti NPLIN metode. NPLIN je metoda laserski indukovane kristalizacije koristeći nefokusirani nanosekundni laserki snop na 532 nm ili 1064 nm. Nekoliko jedinjenja je kristalisano sa NPLINom: urea[1], glicin[2], histidin[3], sirćetna kiselina[4], BPT[5], HEWL[5], KCl[6], $NaClO_3$[7], 5CB[8]. Mehanizam je baziran na nelinearnom Kerrov efektu koji je predlozio Garetz; ova hipoteza je još uvek pod znakom pitanja[9].

S jedne strane, cilj je razumevanje mehanizma nukleacije glicina i histidina u NPLINu, čija selektivna kristalizacija zavisi od polarizacije lasera (linearna ili cirkularna). Ovi eksperimenti su izvedeni pri neutralnom pH. Isproban je efekat spajanja pri različitim pH i uz tešku vodu. Dobro je poznato da niska i visoka pH vrednost[10] i teška voda[11] favorizuju γ polimorfe.

S druge strane, izložili smo karbamazepin NPLINu. Izlaganjem presićenog rastvora laseru uočili smo narandžastu boju izazvanu fotohemijskom reakcijom. Posle nekoliko sati zapažena je i kristalizacija u većini tuba. Po prvi put, pokazali smo da je moguće dobiti kristal karbamazepina koristeći NPLIN tehniku. Eksperimentalna ispitivanja će biti nastavljena u cilju određivanja uticaja lasera na morfologiju kristala.

[1] Garetz et al. Phys. Rev. Lett. vol.77 (1996) n°16, [2] Zaccaro et al. Crystal Growth & Design vol.1 (2001) n°1, 5-8, [3] Sun et al. Crystal Growth & Design vol.8 (2008) n°5, 1720-1722, [4] Ward et al. Phys. Chem. Chem. Phys. Vol.14 (2012) 90 -93, [5] Lee et al. Crystal Growth & Design vol.8 (2008) n°12, 4255-4261, [6] Ward et al. Chemical Physics Letters 481 (2009) 25-28, [7] Ward et al. J. Chem. Phys. Vol. 135 (2011) 114508 [8] Sun et al., Phys. Rev. E vol.79 (2009) 021701, [9] Brandon et al. J. Chem. Phys. Vol. 134 (2011) 154501, [10] Lee et al. Crystal Growth & Design vol.8 (2008) n°1, 108-113 [11] Hughes et al. New J. Chem. Vol.33 (2009) 713–716.

SYNTHESIS AND CRYSTAL STRUCTURE OF DIBROMIDO-(*S,S*)--ETHYLENEDIAMINE-*N,N'*-2-(3-METHYL)BUTANOATO--PLATINUM(IV) COMPLEX

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The title compound was obtained by direct reaction a water solution of $K_2[PtBr_6]$ and tetradentate ligand (*S,S*)-ethylenediamine-*N,N'*-2-(3-methyl)butanoato (*S,S*-eddv) in molar ratio 1:1. The reaction mixture was heated on a stem bath for 12 h, during this period water solution of $LiOH{\cdot}H_2O$ was added. The compound $[PtBr_2(S,S\text{-eddv})]$, as a yellow crystal was separated by filtration, washed with water and air-dried. Yield: 43%.

Crystal data: orthorhombic, space group $P22_12_1$, crystal size 0.503 x 0.405 x 0.359 mm, a = 22.0238(3), b = 20.9314(4), c = 11.5728(2) Å, V = 5334.93(16) Å^3, Z = 4, q_x =2.358 g/cm^3, μ = 12.406 mm^{-1}. The refinement on F^2 (593 parameters and 11054 independent reflections) yielded final R = 0.0270 ($I \geq 2\sigma(I)$), wR = 0.0613, goodness-of-fit on F^2 =1.106, S = 0.998. Ovde postoje dva faktora slaganja (*GOF* ili *S*) sa različitim vrednostima.

Acknowledgement: This work was supported by the ERDF EU grant under the contract No. ITMS26220120047.

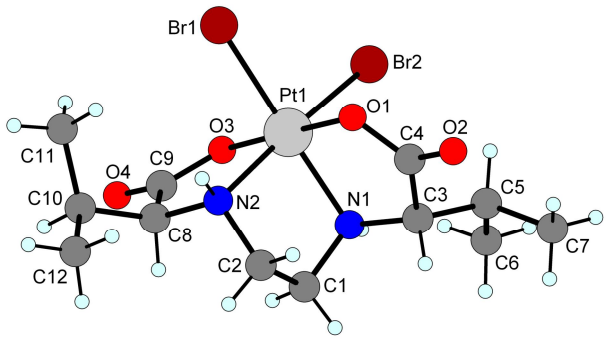

Figure 1. ORTEP plot for molecule of dibromido-(*S,S*)--ethylenediamine-*N,N'*-2-(3-methyl)butanoato-platinum(IV) complex

SINTEZA I KRISTALNA STRUKTURA DIBROMIDO-(*S*,*S*)-ETILENDIAMIN-*N*,*N*′-2--(3-METIL)BUTANOATO-PLATINA(IV) KOMPLEKSA

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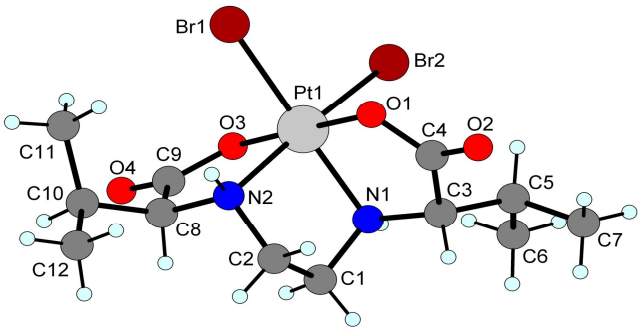
Navedeno jedinjenje dobijeno je direktnom reakcijom između vodenog rastvora $K_2[PtBr_6]$ i tetradentatnog liganda (*S*,*S*)-etilendiamin-*N*,*N*′-2-(3-metil)butanoata u molskom odnosu 1:1. Reakciona smeša je zagrevana na vodenom kupatilu 12 sati uz dodavanje vodenog rastvora $LiOH{\cdot}H_2O$. Jedinjenje [$PtBr_2$(*S*,*S*-eddv)] je kao žuti kristal odvojeno ceđenjem, isprano vodom i sušeno na vazduhu. Prinos 43%.

Kristalografski podaci: ortorombični sistem, prostorna grupa $P22_12_1$, dimenzije kristala 0,503 x 0,405 x 0,359 mm, a = 22,0238(3), b = 20,9314(4), c = 11,5728(2) Å, V = 5334,93(16) Å^3, Z = 4, ρ_x =2,358 g/cm^3, μ = 12,406 mm^{-1}. Utačnjavanje sa F^2 (593 parametara i 11054 nezavisnih refleksija) dalo je R = 0,027 ($I \geq 2\sigma(I)$), wR = 0,0613, $wR(F^2)$ = 1,106 i S = 0,998.

Zahvalnica: Ovaj rad je podržan projektom ERDF EU broj ITMS26220120047.



Slika 1. Struktura dibromido-(*S*,*S*)-etilendiamin-*N*,*N*′-2--(3-metil)butanoato-platina(IV) kompleksa

CRYSTAL AND MOLECULAR STRUCTURE OF 3-*O*-BENZYL-5-*O*-BENZOYL-1,2-*O*-ISOPROPYLIDEN-α-D-GLUCOFURANURONIC ACID NITRILE[1]

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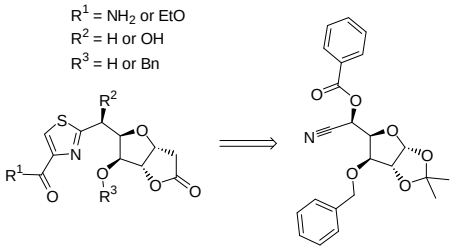
Nitrile **1** (*Scheme* 1.) is the intermediate in the synthesis of several thiazole analogues (**2**) of naturally occurring cytotoxic lactone goniofufurone. Herein we want to report crystal and molecular structure of nitrile **1**.



2 **1**

Scheme 1.

Compound **1** crystallizes in the orthorhombic space group $P2_12_12_1$ with periods a=9.375(5), b=13.754(6), c=16.774(8) Å. Based on measured diffraction intensities, initial structure was determined by direct method (SIR-92) and then anisotropic refined by least square methods (SHELXL-97). Hydrogen atoms were located in geometrically optimal positions which finally resulted in sufficiently reliable agreement between measured (F_o) and calculated (F_c) structure factors R=4.6% for 2861 observed reflections.

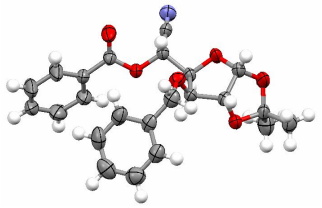


Figure 1. Molecular structure of 3-*O*-benzyl-5-*O*-benzoyl-1,2-*O*-isopropyliden-α-D-glucofuranuronic acid nitrile (1)

[1]The realization of this work was financed by the Ministry of Education and Science of the Republic of Serbia (Grant No. 172006).

KRISTALNA I MOLEKULSKA STRUKTURA NITRILA 3-*O*-BENZIL-5-*O*-BENZOIL-1,2-O-IZOPROPILIDEN-α-D-GLUKOFURANURONSKE KISELINE[1]

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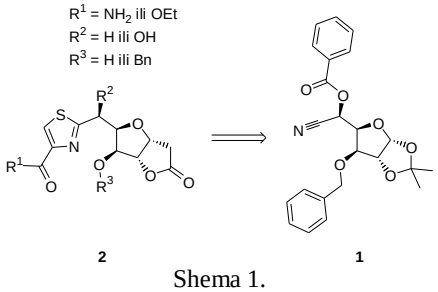
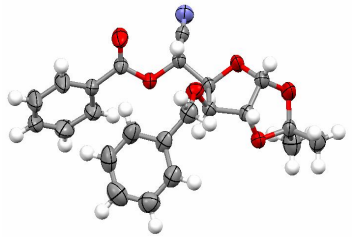
Nitril **1** (*Shema* 1.) je ključni intermedijer u sintezi nekoliko tiazolnih analoga (**2**) citotoksičnog stiril-laktona goniofufurona. U ovom radu želimo da saopštimo kristalnu i molekulsku strukturu nitrila **1**.



Shema 1.

Monokristali jedinjenja **1** pripadaju prostornoj grupi $P2_12_12_1$ sa periodama a=9.375(5), b= 13.754(6), c=16.774(8)Å. Na osnovu izmerenih intenziteta X-difrakcije, polazni model strukture određen je direktnom metodom (SIR-92), a zatim utačnjavan metodom najmanjih kvadrata (SHELXL-97). Atomi vodonika su zadati u geometrijski optimalne položaje što je na kraju rezultiralo dovoljno pouzdanim slaganjem merenih (F_o) i računatih (F_c) modula strukturnih faktora R=4.6% za 2861 opaženih refleksija.



Slika 1. Molekularna struktura nitrila 3-*O*-benzil-5-*O*-benzoil-1,2-*O*-izopropiliden-α-D-glukofuranuronske kiseline (1)

[1]Realizaciju ovog rada finansiralo je Ministarstvo za prosvetu i nauku Republike Srbije (Projekat broj 172006).

MLXH/π INTERACTIONS IN CRYSTAL STRUCTURES

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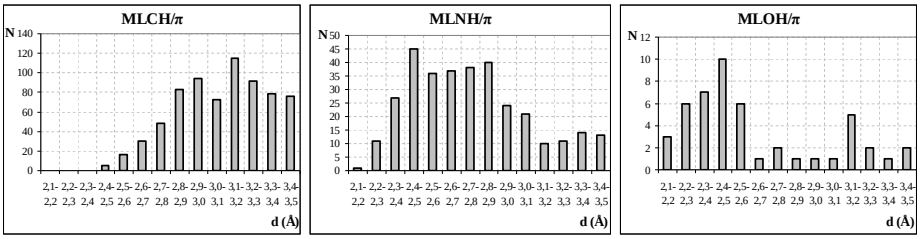
Intensive research on noncovalent interactions involving π systems has shown that these interactions are very important in many fields of chemistry, biochemistry and molecular biology. Bonding interactions between X−H (X = O, N, C) and a π system are called XH/π interactions. These interactions were found in crystal structures of proteins and small molecules. The interactions of coordinated ligands with aromatic rings can also be considered as a special type of XH/π hydrogen bonds, metal-ligand XH/π (MLXH/π) and they have been found in crystal structures of metalloproteins and transition metal complexes.[1,2]

The Cambridge Structural Database (CSD) was screened in order to find interactions between MLXH fragments and phenyl group. We consider that an interaction occurs if the distance between the center of the phenyl ring (Ω) and the hydrogen atom is shorter than 3.5 Å (distance d), while the angle α (X-H···Ω angle) is larger then 110° and angle β (the angle between the H···Ω line and the normal to the chelate ring) is smaller then 30°.



(a) (b) (c)

Histograms of the distribution of values d for (a) MLCH/π, (b) MLNH/π, (c) MLOH/π.

The results of statistical analysis show that MLXH/π interactions with the shortest d distances occur in crystal structures with MLOH/π contacts, while the longest distances are found in crystal structures with MLCH/π contacts. Histograms of the distribution of d values for three types of MLXH/π interactions indicate that the MLOH/π interactions are probably stronger than MLNH/π and MLCH/π interactions. The results of CSD analysis are in agreement with the predicted energies of the OH/π, NH/π and CH/π interactions.

[1] S. D. Zarić, D. Popović, E. W. Knapp, Chemistry – A European Journal, 6 (2000), 3935-3942
[2] G. V. Janjić, M. K. Milčić, S. D. Zarić, Chemical Papers, 63 (2009), 298-305

MLXH/π INTERAKCIJE U KRISTALNIM STRUKTURAMA

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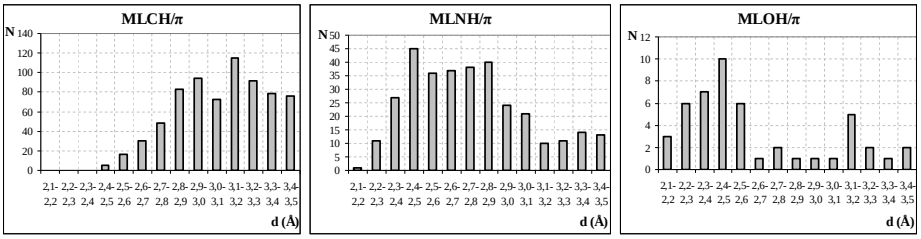
Intenzivna istraživanja nekovalentnih interakcija, koja uključuju π sisteme, pokazala su da su ove interakcije veoma značajne u mnogim oblastima hemije, biohemije i molekularne biologije. Vezivne interakcije između X-H grupe (X=O, N, C) i *π* sistema zovu se XH/π interakcije. Ove interakcije su pronađene u kristalnim strukturama proteina i malih molekula. Interakcije koordinovanih liganada sa aromatičnim prstenovima mogu se posmatrati kao specifičan tip XH/π vodoničnih veza, metal-ligand XH/π (MLXH/*π*) interakcije, a primećene su u kristalnim stukturama metaloproteina i u kompleksima prelaznih metala.[1,2]

U cilju pronalaženja interakcija između MLXH fragmenta i fenil grupe pretražena je Kembrička banka kristalografskih podataka (CSD). Smatra se da se interakcije javljaju ako je rastojanje između centara fenilnog prstena (Ω) i vodonikovog atoma kraće od 3,5 Å (rastojanje d), ako je ugao α (X-H···Ω ugao) veći od 110° i ako je ugao β (ugao između prave H···Ω i normale na ravan prstena) manji od 30°.



(a) (b) (c)

Histogrami raspodele vrednosti d za (a) MLCH/π, (b) MLNH/π, (c) MLOH/π.

Rezultati statističke analize pokazuju da se MLXH/π interakcije sa najkraćim d rastojanjima javljaju u kristalnim strukturama sa MLOH/π kontakatima, dok se najduža d rastojanja javljaju u kristalnim strukturama sa MLCH/π kontaktima. Histogrami raspodele vrednosti d za tri tipa MLXH/π interakcija upućuju na to da su MLOH/π interakcije verovatno jače od MLNH/π i MLCH/π interakcija. Rezultati CSD analiza su u saglasnosti sa predviđenim vrednostima energija za OH/π, NH/π i CH/π interakcije.

[1] S. D. Zarić, D. Popović, E. W. Knapp, Chemistry – A European Journal, 6 (2000), 3935-3942
[2] G. V. Janjić, M. K. Milčić, S. D. Zarić, Chemical Papers, 63 (2009), 298-305

ORIENTATIONS OF AQUA LIGANDS IN CRYSTAL STRUCTURE OF HEXAAQUA-METAL COMPLEXES

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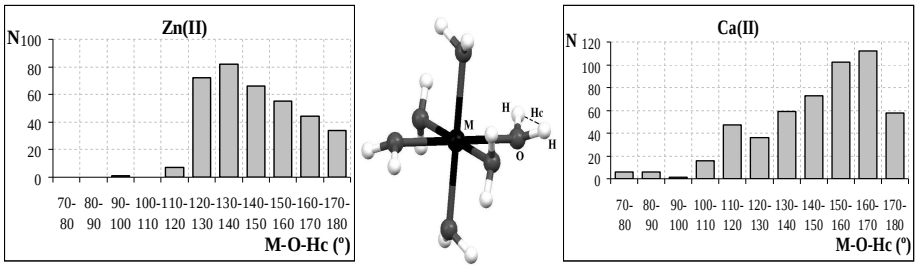
Many properties of complexes depend on orientations of ligands. For example, the orientations of histidines, axially ligated to heme, are considered to have a strong influence on the function of heme cofactors in proteins.[1] The orientation of coordinated molecules or ions depends on crystal field stabilization effects and on intramolecular interactions with other ligands.[2]

In this work, we elucidate the influence of nature of metal ions on mutual orientation of aqua ligands in hexaaqua complexes. The Cambridge Structural Database (CSD) was searched for all hexaaqua complexes of Zn(II) and Ca(II) ions. Orientations of aqua ligands in these complexes, in respect to metal ion, are defined by M-O-Hc angle (see Figure). A comparison of histograms for distribution of M-O-Hc angle values, for Zn(II) and Ca(II) complexes, shows that orientations of aqua ligands do not have the same tendencies. Aqua ligands, in hexaaqua-Zn(II) complexes, have a tendencies to tetrahedral geometry, respect to metal ion. In case of hexaaqua-Ca(II) complexes, aqua ligands prefer the orientations with values of M-O-Hc angle near to 180°. The results show that the orientation of aqua ligands is dependent of metal type in hexaaqua complexes. The results of *ab initio* calculations support this conclusion.



[1] A. A. Rakić, V. B. Medaković, S. D. Zarić, Journal of Inorganic Biochemistry, 100 (2006), 133-142
[2] G. V. Janjić, M. K. Milčić, S. D. Zarić, Chemical Papers, 63 (2009), 298-305

ORIJENTACIJE AKVA LIGANADA U KRISTALNIM STRUKTURAMA HEKSAAKVA KOMPLEKSA METALA

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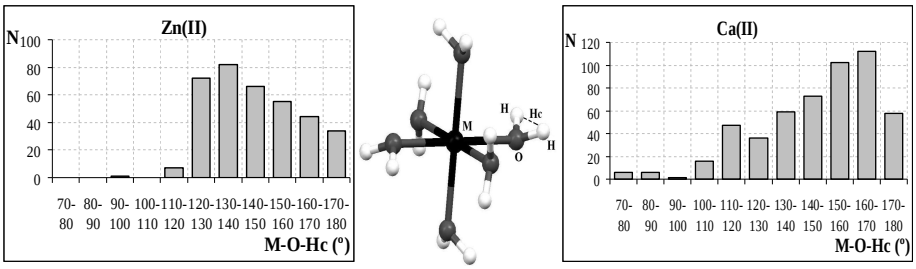
Poznato je da mnoge osobine kompleksa zavise od orijentacije liganada. Na primer, smatra se da orijentacije aksijalno koordinovanih histidina imaju snažan uticaj na funkciju hema u proteinima.[1] Orijentacija koordinovanih molekula ili jona zavisi od efekata stabilizacije kristalnog polja i od intramolekulskih interakcija sa ostalim ligandima.[2]

U ovom radu objasnili smo uticaj prirode jona metala na međusobnu orijentaciju akva liganada u heksaakva kompleksima. Pretražili smo Kembričku banku kristalografskih podataka za sve heksaakva komplekse Zn(II) i Ca(II) jona. Orijentacije akva liganada u ovim kompleksima u odnosu na jon metala definisane su M-O-Hc uglom (Slika). Poređenje histograma raspodela vrednosti M-O-Hc ugla, za Zn(II) i Ca(II) komplekse, ukazuje na različitu tendenciju orijentacije akva liganada. U heksaakva kompleksu Zn(II), postoji težnja liganada ka građenju tetraedarske geometrije u odnosu na jon metala. U slučaju heksaakva kompleksa Ca(II) ligandi preferiraju orijentacije sa vrednostima M-O-Hc ugla bliskim 180°. Rezultati pokazuju da orijentacija akva liganada zavisi od vrste metala u heksaakva kompleksima. Rezultati *ab initio* proračuna u saglasnosti su sa ovim zaključkom.



[1] A. A. Rakić, V. B. Medaković, S. D. Zarić, Journal of Inorganic Biochemistry, 100 (2006), 133–142
[2] G. V. Janjić, M. K. Milčić, S. D. Zarić, Chemical Papers, 63 (2009), 298–305

INTERACTIONS BETWEEN TWO BENZENE MOLECULES IN SANDWICH COMPOUNDS

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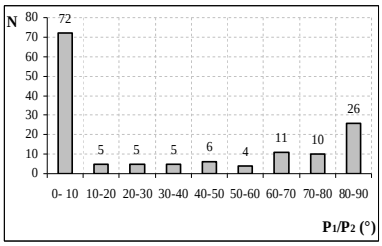
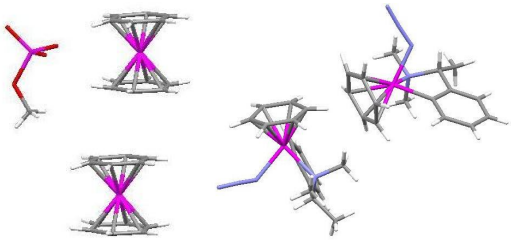
Aromatic-aromatic interactions are of great importance in numerous molecular systems, from biomolecules to molecular crystals.[1] Aromatic interactions between two benzene molecules were extensively studied.[2]

Here, we present analysis on interactions between two benzene molecules in sandwich compounds. Analysis is based on crystal structures from Cambridge Structural Database (CSD). We consider that the interaction between two benzene ligands occurs if the distance between centroids of the rings is smaller than 5.7 Å. By searching the CSD, using the described criteria, 144 contacts of benzene ligands were found. The results of analysis show that most of these contacts form parallel interactions, with maximum of P_1/P_2 angle distribution (the angle between two planes of benzene rings) in the range from 0° to 10°. Most of these contacts form stacking interactions, Different than noncoordinated benzene molecules that usually form parallel interactions with large offsets.[2] The number of contacts with CH/π interactions (the values of P_1/P_2 angle are in the range from 60 to 90°), is much smaller than number of contacts with parallel interactions.





[1] L. M. Salonen, M. Ellermann, F. Diederich, Angew. Chem. Int. Ed., 50 (2011), 4808-4842
[2] D. B. Ninković, G. V. Janjić, D. Ž. Veljković, D. N. Sredojević, S. D. Zarić, ChemPhysChem, 12 (2011), 3511-3514

INTERAKCIJE IZMEĐU DVA MOLEKULA BENZENA U SENDVIČ-JEDINJENJIMA

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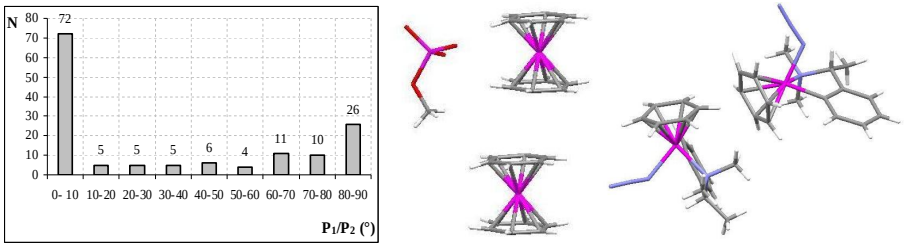
Aromatično-aromatične interakcije su od velikog značaja u brojnim molekulskim sistemima, od biomolekula do molekulskih kristala.[1] Aromatične interakcije između dva molekula benzena intenzivno su ispitivane.[2]

Ovde su prikazani rezultati analize interakcija između dva molekula benzena u sendvič-jedinjenjima. Analiza je zasnovana na kristalnim strukturama dobijenim pretraživanjem Kembričke banke kristalografskih podataka (CSD). Interakcije između dva molekula benzena kao liganda javljaju se ukoliko je rastojanje između centroida prstenova manje od 5,7 Å. Pretragom CSD, uz korišćenje opisanog kriterijuma, pronašli smo 144 kontakta između benzena kao liganada. Rezultati analize pokazuju da većina ovih kontakata predstavlja paralelne interakcije, sa maksimumom raspodele P_1/P_2 ugla (ugao između ravni dva prstena benzena) u opsegu od 0° do 10°. U većini opisanih slučajeva dolazi do formiranja steking interakcija, za razliku od nekoordinovanih molekula benzena. Slobodni molekuli benzena formiraju paralelne interakcije, ali na velikim horizontalnim pomeranjima.[2] Broj kontakata koji formiraju CH/π interakcije (vrednosti P_1/P_2 ugla u opsegu od 60° do 90°), znatno je manji od broja kontakata koji formiraju paralelne interakcije.



[1] L. M. Salonen, M. Ellermann, F. Diederich, Angew. Chem. Int. Ed., 50 (2011), 4808-4842
[2] D. B. Ninković, G. V. Janjić, D. Ž. Veljković, D. N. Sredojević, S. D. Zarić, ChemPhysChem, 12 (2011), 3511-3514

STACKING INTERACTIONS OF [Ni(acac)$_2$] COMPLEX AND BENZENE. QUANTUM-CHEMICAL ANALYSIS OF THE INTERACTIONS

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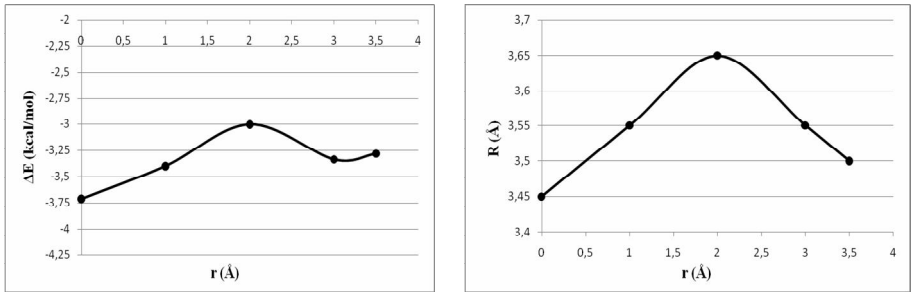
The analysis of crystal structures from Cambridge Structural Database (CSD) show that there are stacking interactions between chelate and C_6-aromatic rings.[1] Statistical analysis of the geometrical parameters in the crystal structure of the square-planar transition metal complexes show that the geometry of the stacking interaction between C_6-aromatic and chelate rings is similar to the geometry of the stacking interaction of two benzene rings.[1]

In this work the energies of stacking interactions of [Ni(acac)$_2$] with benzene were obtained by the quantum chemical calculations using SCS-MP2//def2-TZVP level of theory; effective core potential was used for the nickel atom (SDD). The calculated energies of stacking interactions of benzene with Ni(*acac*) chelate are two times stronger that the stacking energies of two benzene rings.[2]



(a) (b)

The calculated interaction energies (ΔE) for [Ni(*acac*)$_2$]– benzene system (a) and optimal normal distances R (b), plotted as a function of *offset* value r.

These results can be very important for various systems. For example, in supramolecular chemistry incorporating square-planar metal complexes, which possess chelate rings with delocalized bonds in stacking interactions, should stabilize systems significantly.

[1] Z. D. Tomić, D. N. Sredojević and S. D. Zarić, Cryst. Growth Des. 6 (2006) 29-31
[2] D. B. Ninković, G. V. Janjić, D. Ž. Veljković, D. N. Sredojević, S. D. Zarić, ChemPhysChem 12 (2011) 3511-3514.

STEKING INTERAKCIJE [Ni(acac)$_2$] KOMPLEKSA I BENZENA. KVANTNO-HEMIJSKA ANALIZA INTERAKCIJA

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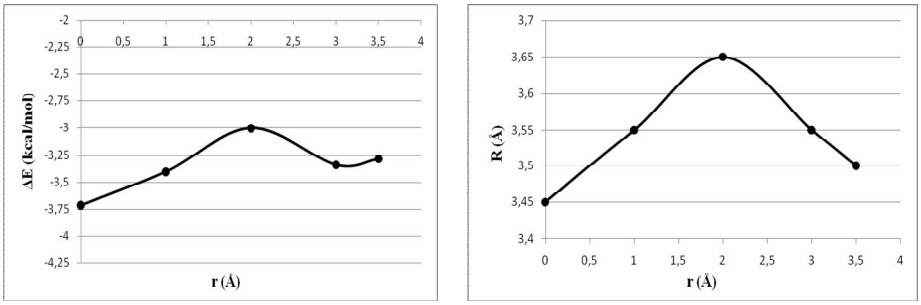
Analizom podataka dobijenih pretraživanjem Kembričke banke kristalografskih podataka (CSD) pokazano je da postoje steking interakcije između helatnih i C_6–aromatičnih prstenova u kristalnim strukturama.[1] Statistička analiza geometrijskih parametara u kristalnim strukturama kvadratno-planarnih kompleksa prelaznih metala ukazala je na to da su interakcije između C_6–aromatičnih i helatnih prstenova slične steking interakcijama između dva molekula benzena.[1]

U ovom radu energije steking interakcija [Ni(*acac*)$_2$] kompleksa i benzena su izračunate korišćenjem SCS-MP2/def2-TZVP nivoa teorije; efektivni potencijal jezgra je korišćen za atom nikla (SDD). Izračunate vrednosti energija steking interakcija između benzena i Ni(*acac*) – helata dvostruko su veće od vrednosti energija interakcija između dva molekula benzena.[2]



(a) (b)

Izračunate vrednosti energija interakcija (ΔE) za sistem [Ni(*acac*)$_2$]–benzen (a) i optimalna normalna rastojanja R (b), u funkciji vrednosti r.

Ovi rezultati mogu biti od značaja za različite sisteme. Na primer, u supramolekulskoj hemiji, uključivanje kvadratno-planarnih kompleksa prelaznih metala, koji poseduju helatne prstenove sa delokalizovanim vezama, u steking interakcije moglo bi dovesti do značajne stabilizacije sistema.

[1] Z. D. Tomić, D. N. Sredojević, S. D. Zarić, Cryst. Growth Des., 6 (2006), 29-31
[2] D. B. Ninković, G. V. Janjić, D. Ž. Veljković, D. N. Sredojević, S. D. Zarić, ChemPhysChem, 12 (2011), 3511-3514

STRONG HYDROGEN BONDS OF COORDINATED WATER. INFLUENCE OF METAL CATION ON WATER HYDROGEN BONDS

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Water plays an essential role in chemical structures and processes in various systems, from materials to biology. Small size and high polarity govern water capabilities and the complexity of its behaviour. Most important is its hydrogen bonding ability, as water forms strong hydrogen bonds to other polar molecules and builds strong networks with itself.[1-3]

In this work the influence of water coordination to a metal cation on water hydrogen bonds was studied by analyzing crystal structures from Cambridge Structural Database and by high level *ab initio* calculations. The hydrogen bonds of the water molecules in the first hydration shell of the cation were compared with the hydrogen bonds of free water molecules. To the best of our knowledge, this is the first work reporting on the strength of the hydrogen bonds of the first hydration shell of metal cations based on the data in the crystal structures from the CSD. Positively charged complexes form quite strong hydrogen bonds, the hydrogen bond energy of $[Zn(H_2O)_6]^{2+}$ complex is -21.89 kcal/mol, which is several times stronger than the hydrogen bond of non-coordinated water, -4.77 kcal/mol.

Hence, the presence of a cation changes remarkably the strength of hydrogen bonds. Moreover, the hydrogen bond of aqua ligand has a strong influence on the stability and coordination number of a complex. The results can be important for all the systems where a water molecule is in contact with metal cations, from biomolecules to materials.

[1] W. M. Latimer, W. H. Rodebush, J. Am. Chem. Soc., 42 (1920), 1419-1433
[2] L. Pauling, J. Am. Chem. Soc., 57 (1935), 2680-2684
[3] M. L. Huggins, J. Org. Chem., 1 (1937), 407-456

JAKE VODONIČNE VEZE KOORDINOVANOG MOLEKULA VODE. UTICAJ JONA METALA NA JAČINU VODONIČNE VEZE

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Voda ima veoma značajnu ulogu u formiranju različitih struktura kao i u brojnim procesima u biološkim sistemima. Svojstva molekaula vode i kompleksno ponašanje posledica su male veličine i visoke polarnosti molekula vode. Jedna od najznačajnijih karakteristika molekula vode je sposobnost vodoničnog vezivanja za druge polarne molekule kao i formiranje mreže vodoničnih veza između samih molekula vode.[1-3]

U ovom radu ispitivan je uticaj koordinacije vode za jon metala na vodonično vezivanje molekula vode, analizom podataka dobijenih iz Kembričke banke kristalografskih podataka kao i *ab initio* proračunima visokog nivoa. Poređena je jačina vodonične veze između koordinovanog i nekoordinovanog molekula vode sa jačinom vodonične veze između dva nekoordinovana molekula vode. Prema našim saznanjima, u ovom radu je po prvi put ispitivana jačina vodoničnih veza koju grade molekuli vode u prvoj koordinacionoj sferi, na osnovu analize kristalnih struktura iz CSD-a. Pozitivno naelektrisani kompleksi formiraju veoma jake vodonične veze. Energija vodonične veze za kompleks $[Zn(H_2O)_6]^{2+}$ iznosi -21,89 kcal/mol, što je nekoliko puta jače od vodonične veze koju grade nekoordinovani molekuli vode (-4,77 kcal/mol).

Dobijeni rezultati jasno ukazuju da prisustvo jona metala značajno utiče na jačinu vodonične veze. Takođe, vodonične veze koje grade koordinovani molekuli vode značajno utiču na stabilnost kompleksa i njegov koordinacioni broj. Ovi rezultati mogu biti od značaja za sve sisteme gde su molekuli vode u kontaktu sa jonima metala, od biomolekula do materijala.

[1] W. M. Latimer, W. H. Rodebush, J. Am. Chem. Soc., 42 (1920), 1419-1433
[2] L. Pauling, J. Am. Chem. Soc., 57 (1935), 2680-2684
[3] M. L. Huggins, J. Org. Chem., 1 (1937), 407-456

PARALLEL INTERACTIONS BETWEEN PORPHYRINATO LIGANDS IN CRYSTAL STRUCTURE OF SQUARE-PLANAR METAL COMPLEXES

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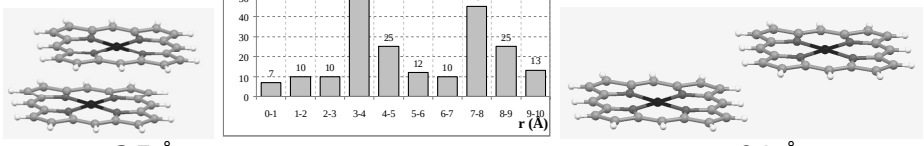
Stacking interactions between aromatic organic molecules or fragments are extensively studied.[1] However, it was shown that other planar molecules and fragments can also be involved in stacking interactions. Chelate rings with delocalized π-system can form stacking interactions[2] in similar way as organic aromatic rings.[1]

We studied the parallel interactions of square-planar porphyrinato complexes in crystal structures by analyzing the data from Cambridge Structural Database. In order to find intermolecular parallel interactions, we used the criterion where the distance between metal ions was below 10.0 Å. The mutual orientations of the interacting complexes were analyzed using r parameter (the distance between the metal ion of the first complex (M_1) and the projection of the metal ion of the second complex (M_2) onto the average plane of the first one).

The distribution of the offset r values reveals that most of contacts have offset values in the range 3.0-4.0 Å, which corresponds to stacking interactions. The results of statistical analysis show unexpectedly large number of contacts with r value larger than 7.0 Å, which corresponds to parallel interactions at large offsets.



r=3.7 Å r=9.2 Å

[1] D. B. Ninković, G. V. Janjić, D. Ž. Veljković, D. N. Sredojević, S. D. Zarić, ChemPhysChem, 12 (2011), 3511-3514
[2] G. V. Janjić, J. M. Andrić, A. Kapor, Ž. D. Bugarčić, S. D. Zarić, CrystEngComm, 12 (2010), 3773-3779

PARALELNE INTERAKCIJE IZMEĐU PORFIRINSKIH LIGANADA U KRISTALNIM STRUKTURAMA KVADRATNO-PLANARNIH KOMPLEKSA METALA

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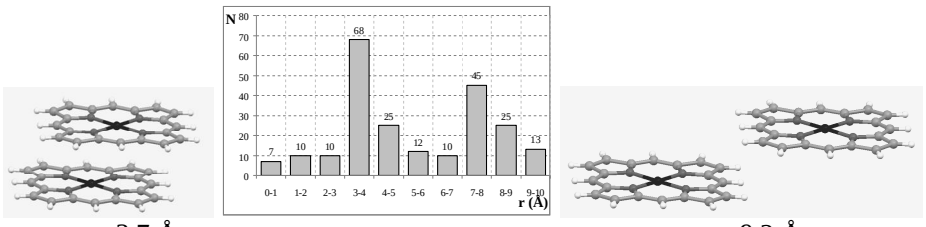
Steking interakcije između aromatičnih organskih molekula ili fragmenata intenzivno su proučavane.[1] Međutim, pokazano je da i drugi planarni molekuli i njihovi fragmenti mogu da grade steking interakcije. Publikovane su brojne studije u kojima helatni prstenovi, sa delokalizovanim π-sistemom, formiraju steking interakcije,[2] na način sličan aromatičnim organskim molekulima.[1]

Proučavali smo paralelne interakcije kvadratno-planarnih porfirinskih kompleksa u kristalnim strukturama, analizirajući podatke dobijene pretragom Kembričke banke kristalografskih podataka. U cilju pronalaženja intermolekulskih paralelnih interakcija, kao granični kriterijum korišćeno je rastojanje između jona metala, manje od 10 Å. Analizirana je međusobna orijentacija intereagujućih kompleksa korišćenjem parametra r (koji predstavlja rastojanje između jona metala jednog kompleksa (M_1) i projekcije jona metala drugog kompleksa (M_2), na ravan prvog kompleksa).

Raspodela ofset vrednosti (r) pokazala je da većina kontakata imaju ofset vrednosti od 3,0 do 4,0 Å, što odgovara steking interakcijama. Rezultati statističke analize pokazuju neočekivano veliki broj kontakta sa vrednošću parametra r većom od 7 Å, što odgovara paralelnim interakcijama na velikim horizontalnim pomeranjima.



r=3,7 Å r=9,2 Å

[1] D. B. Ninković, G. V. Janjić, D. Ž. Veljković, D. N. Sredojević, S. D. Zarić, ChemPhysChem, 12 (2011), 3511-3514
[2] G. V. Janjić, J. M. Andrić, A. Kapor, Ž. D. Bugarčić, S. D. Zarić, CrystEngComm, 12 (2010), 3773-3779

MOLECULAR AND CRYSTAL STRUCTURES OF NOVEL STYRYL LACTONES

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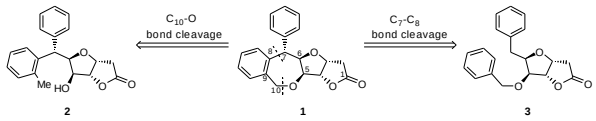
The styryl lactones are a group of secondary metabolites that has been isolated from the genus *Goniothalamus*. They have unique structural features and demonstrate interesting biological activities. They also show a moderate to potent antitumour activity. In our laboratory we have carried out the synthesis of new styryl lactones (**2** and **3**) designed according to previously obtained oxepane analogue **1** (*Scheme 1.*)[1] and completed the structural characterisation of the obtained crystalline derivative **2** and **3**.



Scheme 1. Design of analogues **2** and **3**

Figure 1. Molecular structures of analogues **2** and **3**

Compounds crystallized from CH_2Cl_2/hexane and both of them crystallize in the monoclinic space group $P2_1$. Based on measured X-diffraction intensities, position of C and O atoms in elementary cells were determined by direct method (SIR-92) and then refined by least square methods (SHELXL-97) in anisotropical thermal approximation, while the positions of H atoms were set geometrically with the possibility of refinement of isotropic thermal vibrations whose intensity depended on the type of hybridization (*Picture 1.*). Basic crystallographic data and refinement results are the following:
2: $C_{20}H_{20}O_4$, Z=2, a=7.7334(3), b=32.0687(14), c=7.0404(5)Å, β=90.03(7)°, V=1746.02 Å^3, $P2_1$, R=6.2%, S=0.86, Δρ -0.122, +0.095.
3: $C_{20}H_{20}O_4$, Z=2, a=8.309(5), b=5.468(5), c=18.794(5)Å, β=94.40(5),° V=851.4(8) Å^3, $P2_1$, R= 3.6%, S=0.81, Δρ -0.143, +0.129.

The biological activity analysis has been shown that both compounds exibit a potent cytotoxicity towards selected human tumour cell lines.

The work was supported by the Ministry of Education and Sciences of the Republic of Serbia (Project No. 172006).

[1] Francuz, J.; Srećo, B.; Popsavin, M.; Benedeković, G.; Divjaković, V.; Kojić, V.; Bogdanović, G.; Kapor, A.; Popsavin, V. Tetrahedron Letters, 53 (2012), 1819.

MOLEKULSKE I KRISTALNE STRUKTURE NOVIH STIRIL-LAKTONA

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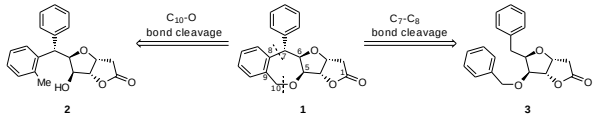
Stiril-laktoni predstavljaju grupu sekundarnih metabolita uglavnom izolovanih iz roda *Goniothalamus*. Posebna pažnja je fokusirana na visoko citotoksične i anti-tumorske karakteristike ovih supstanci. Pored značajne biološke aktivnosti imaju i interesantne strukturne karakteristike. U našoj laboratoriji su realizovane sinteze novih stiril-laktona (**2** i **3**) dizajniranih prema prethodno dobijenom oksepanskom analogu **1** (Shema 1.)[1], kao i rendgenostrukturna karakterizacija dobijenih kristalnih derivata **2** i **3**.



Shema 1. Dizajn analoga **2** i **3**.

Slika 1. Molekulske strukture analoga **2** i **3**.

Jedinjenja su kristalisala iz rastvora CH_2Cl_2/heksan i oba pripadaju monoklinskom sistemu ($P2_1$). Na osnovu izmerenih intenziteta X-difrakcije, položaji atoma C i O u elementarnoj ćeliji odredjeni su direktnom metodom, a zatim utačnjavani metodom najmanjih kvadrata (SHELXL-97) u anizotropnoj termičkoj aproksimaciji, dok su položaji H atoma bili zadati geometrijski uz mogućnost utačnjavanja izotropnih termičkih vibracija čiji intenzitet je zavisio od tipa hibridizacije (Slika 1.). Osnovni kristalografski podaci, kao i neki od parametara utačnjavanja za **2** i **3** su sledeći:

2: $C_{20}H_{20}O_4$, Z=2, a=7.7334(3), b=32.0687(14), c=7.0404(5)Å, β=90.03(7)^o, V=1746.02 Å^3, $P2_1$, R=6.2%, S=0.86, Δρ -0.122, +0.095.

3: $C_{20}H_{20}O_4$, Z=2, a=8.309(5), b=5.468(5), c=18.794(5)Å, β=94.40(5),° V=851.4(8) Å^3, $P2_1$, R= 3.6%, S=0.81, Δρ -0.143, +0.129.

Analize bioloških aktivnosti pokazale su da oba molekula ispoljavaju snažnu *in vitro* citotoksičnost prema ćelijskim linijama odabranih humanih tumora.

Realizaciju ovog rada finansiralo je Ministarstvo za prosvetu i nauku Republike Srbije (Projekat 172006).

[1] Francuz, J.; Srećo, B.; Popsavin, M.; Benedeković, G.; Divjaković, V.; Kojić, V.; Bogdanović, G.; Kapor, A.; Popsavin, V.; Tetrahedron Letters, 53 (2012), 1819.

FLUX GROWN $\tilde{\beta}$- AND $\tilde{\gamma}$-SPODUMENE SINGLE CRYSTALS

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In the scope of our ongoing study of migrational dynamics in Li-aluminosilicates, we have successfully synthesized the tetragonal and hexagonal modifications of $LiAlSi_2O_6$. The flux technique was applied for the growth of β- and γ-spodumene single crystals. Li_2CO_3, Al_2O_3 and SiO_2 were used as starting materials, while $LiVO_3$ was used as a flux with nutritient-to-flux ratio of 1:9. The mixture was heated and held at 1100 ºC for 24 h in order to homogenize the melt. Afterwards, the mixture was slowly cooled down to 700 ºC in order for $LiAlSi_2O_6$ to crystallize. In the end, the obtained crystals were removed from the polycrystalline $LiVO_3$ matrix by dissolving and rinsing the vanadate matrix in warm water. SEM results show that we have obtained two different types of crystals. Large hexagonal crystals (length ≈ 1 – 2 mm) are γ-spodumene. About ten times smaller pseudo-cubic crystals (length ≈ 0.2 mm) are β-spodumenes. Both polymorphs were confirmed by Raman spectroscopy. The average chemical formula of all analyzed crystals obtained by EDX analysis is $Li_{0.78}Al_{0.78}Si_{2.22}O_6$. Sufficiently large single crystals, ~ 2 mm in diameter, shall be used for conductivity analyses and results compared with the known data on Li-dynamics in natural monoclinic $LiAlSi_2O_6$.

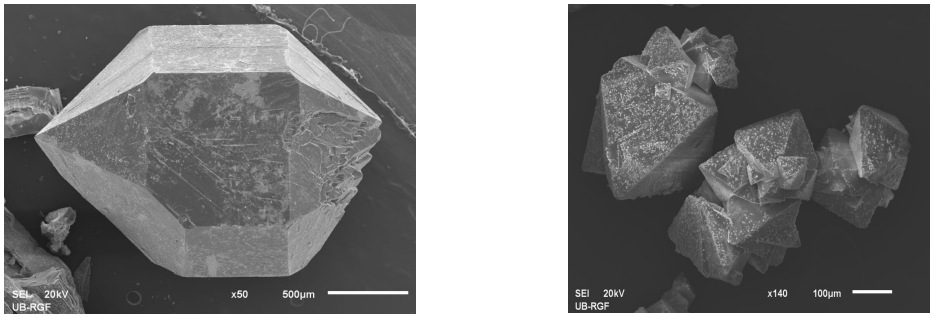

Figure 1. The SEM images of: a) γ-spodumene hexagonal crystal - hexagonal prism in combination with hexagonal bipyramid; b) β-spodumene crystals with pseudo-cubic simmetry.

SINTEZA MONOKRISTALA $\tilde{\beta}$- I $\tilde{\gamma}$-SPODUMENA METODOM FLUKSA

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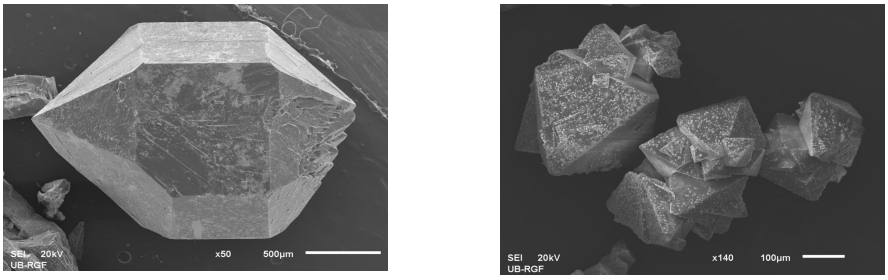
U okviru proučavanja migracione dinamike u litijumskim alumosilikatima, uspešno su sintetisane dve polimorfne modifikacije $LiAlSi_2O_6$. Za sintezu monokristala β- and γ-spodumena primenjena je metoda fluksa. Kao početni reagensi korišćeni su Li_2CO_3, Al_2O_3 and SiO_2, dok je kao fluks upotrebljen $LiVO_3$ pri čemu je odnos iznosio 1:9. Dobijena mešavina je zagrevana i držana 24 h na temperaturi od 1100 °C kako bi došlo do stapanja i potpune homogenizacije. Nakon toga, mešavina je polako hlađena do temperature 700 °C da bi $LiAlSi_2O_6$ kristalisao. Na ovaj način su dobijeni kristali koji su iz matrice fluksa izvađeni rastvaranjem u toploj vodi. Rezultati SEM analiza su pokazali da su dobijene dve različite vrste kristala. Veći heksagonalni kristali (dužine ≈ 1 – 2 mm) predstavljaju γ-spodumene, dok su oko deset puta manji kristali (≈ 0,2 mm) zapravo pseudo-teseralni kristali β-spodumena. Prisustvo oba polimorfa potvrđeno je Ramanskom spektroskopijom. EDX analizom je dobijena prosečna hemijska formula sintetisanih kristala i može se predstaviti na sledeći način: $Li_{0,78}Al_{0,78}Si_{2,22}O_6$. Veliki kristali, dužine oko 2 mm, biće dalje korišćeni za analizu provodnosti, a dobijeni razultati će biti upoređeni sa poznatim podacima za prirodni monoklinični $LiAlSi_2O_6$.



Slika 1. SEM mikrofotografija: a) heksagonalnih kristala γ-spodumena (heksagonalna prizma u kombinaciji sa heksagonalnom bipiramidom); b) pseudo-teseralnih kristala β-spodumena.

CRYSTAL AND MOLECULAR STRUCTURE OF SOME NEWLY SYNTHESIZED 6-*O*-CINNAMOYL DERIVATIVES OF CRASSALACTONE D AND OF ITS 4-EPIMER

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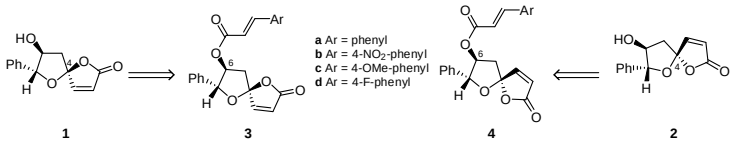
Crassalactone D (**1**; Scheme 1.), naturally occurring styryl-lactone [1] that shows remarkable antiproliferative activity, was used as a lead for design and synthesis of 6-*O*-cinnamoyl derivatives of **1** (compounds **3a-d**) and of its 4-epimer **2** (compounds **4a-d**). Herein we want to report crystal and molecular structure of compounds **3b-d** and **4a**.



Scheme 1.

Compounds **4a** and **3c** crystallize in the same orthorhombic space group $P2_12_12_1$ with approximately equal volume of elementary cells, while molecules **3b** and **3d** crystallize in triclinic space group *P*1 with approximately equal volume of elementary cells. Based on measured diffraction intensities, initial structures were determined by direct method (SIR-92) and then anisotropic refined by least square methods (SHELXL-97). Hydrogen atoms were located in geometrically optimal positions which finally resulted in sufficiently reliable agreement between measured and calculated structure factors.

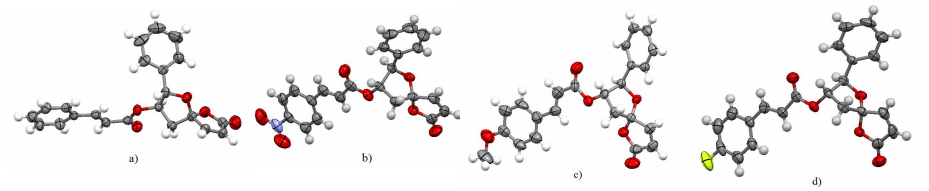


Figure 1. a) Molecular structure of 6-*O*-cinnamoyl-4-*epi*-crassalactone D (**4a**); b) 6-*O*-*p*-nitrocinnamoyl-crassalactone D (**3b**); c) 6-*O*-*p*-methoxycinnamoyl-crassalactone D (**3c**) and d) 6-*O*-*p*-fluorocinnamoyl-crassalactone D (**3d**).

The work was supported by the Ministry of Education and Science of the Republic of Serbia (Project No. 172006).

[1] P. Tuchinda, B. Munyoo, M. Pohmakotr, P. Thinapong, S. Sophasan, T. Santisuk, V. Reutrakul, J. Nat. Prod., 69 (2006), 1728.

KRISTALNA I MOLEKULSKA STRUKTURA NEKIH OD NOVOSINTETIZOVANIH 6-*O*-CINAMOIL DERIVATA KRASALAKTONA D I NJEGOVOG 4-EPIMERA

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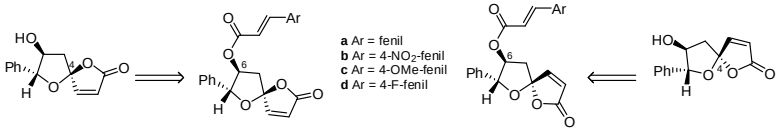
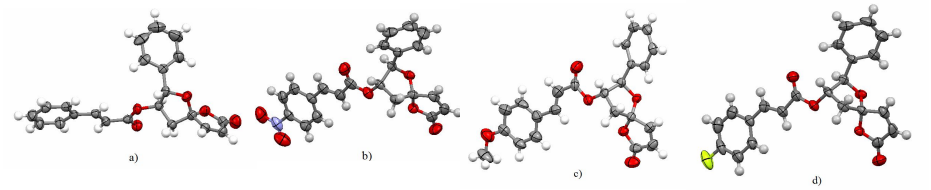
Krasalakton D (**1**, *Shema 1.*), prirodni stiril-lakton[1] koji pokazuje značajnu biološku aktivnost, poslužio je kao "lead compound" za dizajn i sintezu 6-*O*-cinamoil derivata **1** (molekuli **3a-d**) i njegovog 4-epimera **2** (molekuli **4a-d**). U ovom radu želimo da saopštimo kristalne i molekulske strukture supstanci **3b-d** i **4a**.



Shema 1.

Monokristali jedinjenja **4a** i **3c** pripadaju prostornoj grupi $P2_12_12_1$ sa periodama koje određuju približno podjednake zapremine elementarnih ćelija, dok monokristali jedinjenja **3b** i **3d** imaju najnižu simetriju (grupa $P1$) sa, takođe, međusobno sličnim zapreminama elementarnih ćelija. Na osnovu izmerenih intenziteta rendgenske difrakcije, polazni modeli struktura određeni su direktnom metodom (SIR-92), a zatim utačnjavani metodom najmanjih kvadrata (SHELXL-97). Atomi vodonika su zadati u geometrijski optimalne položaje što je na kraju rezultiralo dovoljno pouzdanim slaganjem merenih (F_o) i računatih (F_c) modula strukturnih faktora.



Slika 1. a) Molekulske strukture 6-O-cinamoil-4-epi-krasalakton D (**4a**); b) 6-O-p-nitrocinamoil-krasalaktona D (**3b**); c) 6-O-p-metoksicinamoil-krasalaktona D (**3c**) i d) 6-O-p-fluorocinamoil-krasalaktona D (**3d**).

Realizaciju ovog rada finansiralo je Ministarstvo prosvete i nauke Republike Srbije (projekat 172006).

[1] P. Tuchinda, B. Munyoo, M. Pohmakotr, P. Thinapong, S. Sophasan, T. Santisuk, V. Reutrakul, J. Nat. Prod., 69 (2006), 1728.

CRYSTAL STRUCTURES AND NA^+/K^+ ATPASE INHIBITION PROPERTIES OF FUNCTIONALIZED HEXAVANADATE: A NEW SERIES WITH PROMISING PROPERTIES

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Hexavanadate (V6), an important series of polyoxovanadates (POVs), are sensitive and highly unstable compounds. Therefore, functionalization with organic groups through covalent bonding with the V6 core gives stable compounds, leading to a majority of crystalline structures of functionalized hexavanadates [1]. In order to determine the influence of organic segment on the POV core, we have synthesized a new series of esterificated hexavanadates with carbon chains of different lengths [2].

Classical crystalline structures had been studied for $[V6\text{-}C3]^-[Bu]^+$, $[V6\text{-}C6]^-[Bu]^+$, $[V6\text{-}C18]^-[Bu]^+$. For $[V6\text{-}C3]^-[Bu]^+$, there is an interesting supramolecular assembly originating from the hydrogen bonding interactions between the terminal oxygen of the V6 cluster and the tris(alkoxo) ligands. The two adjusted polyanions are linked by a couple of C-H...O hydrogen bonds and form a 1D chain parallel to the crystallographic *a* axis.

We have focused on the bioactivity of functionalized hexavanadates because vanadium exhibits a relative low toxicity in biological media. POVs interact with biomolecules of various and versatile activity (enzyme inhibitor or activator), especially the Na^+/K^+ ATPase inhibition. We have tested the influences of functionalized hexavanadates on Na^+/K^+ ATP-ase and ecto-ATPase activities. Some of them present at concentrations higher than 0.1 mmol/l completely inhibited Na^+/K^+ ATP-ase and more than 50% of ecto-ATPase activity. These results are important in the context of the various biological applications and stand for promising properties in pharmaceutical chemistry.

Furthermore, charge density studies on functionalized hexavanadates will be determined in the future, and will give a better understanding to research the relationship between experimental electrostatic properties of the different V6 and their bioactivities.

[1] see for example a) D. Charles, H. Hans. J. Am. Chem. Soc, (2005), 127, 13978-13987 b) C. Qin, J. Zubieta. Inorg. Chem., (1990), 29, 1456-1458
[2] a) P. C. Yin, P. F. Wu, Z. C. Xiao, D. Li, E. Bitterlich, J. Zhang, P. Cheng, D. V. Vezenov, T. B. Liu, Y. G. Wei. Angew. Chem. Int . Ed., (2011), 50, 2521–2525 b) P. F. Wu, Z. C. Xiao, J. Zhang, J. Hao, J. K.Chen,; P. C. Yin, Y. G. Wei. Chem. Commun., (2011), 47, 5557-5559

KRISTALNE STRUKTURE I KARAKTERISTIKE INHIBICIJE NA^+/K^+ ATPAZE FUNKCIONALIZOVANIM HEKSAVANADATIMA: NOVE KLASE SA OBEĆAVAJUĆIM OSOBINAMA

Xiao Xu[a], Nada Bošnjaković-Pavlović [b], Danijela Krstić [c], Mirjana Čolović [d], Vesna Vasić [d], Pingfan Wu [e], Yongge Wei [e], Anne Spasojević-de Biré [a]

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Heksavanadati (V6), veoma značajna klasa polioksovanadata, POVa, su osetljiva i veoma nestabilna jedinjenja, koja funkcionalizacijom sa organskim grupama kroz kovalentne veze sa V6 jezgrom daju stabilna jedinjenja [1]. U cilju određivanja uticaja organskih segmenata na POV jezgro, mi smo sintetisali novu seriju esterifikovanih heksavanadata sa različitim dužinama ugljeničnih lanaca [2].

Kristalne strukture određene su za $[V6\text{-}C3]^-[Bu]^+$, $[V6\text{-}C6]^-[Bu]^+$, $[V6\text{-}C18]^-[Bu]^+$. Utvrđeno je da molekuli $[V6\text{-}C3]^-[Bu]^+$ formiraju interesantno supermolekulsko uređenje zasnovano na vodoničnim vezama između terminalnog kiseonika V6 klastera i tris (alkokso) liganda. Dva polianjona su povezana parom C-H...O vodoničnih veza i formiraju 1D lanac paralelan kristalograskoj osi *a* .

Mi smo se orjentisali na biološku aktivnost funkcionalnih heksavanadata jer vanadium ima relativno nisku toksičnost u biološkim sistemima. POVi interaguju sa biomolekulima različitom i raznovrsnom aktivnošću (inhibicija ili aktivacija enzima), posebno inhibirajući Na^+/K^+ ATPazu. Testirali smo uticaj funkcionalnih heksavanadata na aktivnost Na^+/K^+ ATP-aze i ekto-ATPaze. Neki od njih pri koncentracijama većim od 0.1 mmol/l kompletno inhibiraju Na^+/K^+ ATP-azu i vise od 50% ecto-ATPaze. Ovi rezultati su veoma značajni za objašnjenje biološke aktivnosti i sa gledišta primene u farmaceutskoj hemiji.

Štaviše, planirana je i analiza elektronske gustine funkcionalnih heksavanadata koja će omogućiće bolje razumevanje veze između eksperimentalno određenih elektrostatičkih osobina različitih V6 i njihove biološke aktivnosti.

[1] see for example a) D. Charles, H. Hans. J. Am. Chem. Soc, (2005), 127, 13978-13987 b) C. Qin, J. Zubieta. Inorg. Chem., (1990), 29, 1456-1458

[2] a) P. C. Yin, P. F. Wu, Z. C. Xiao, D. Li, E. Bitterlich, J. Zhang, P. Cheng, D. V. Vezenov, T. B. Liu, Y. G. Wei. Angew. Chem. Int . Ed., (2011), 50, 2521–2525 b) P. F. Wu, Z. C. Xiao, J. Zhang, J. Hao, J. K.Chen,; P. C. Yin, Y. G. Wei. Chem. Commun., (2011), 47, 5557-5559

PREDICTION OF INTERACTION SITE OF A DRUG. A COMBINED APPROACH USING HIGH RESOLUTION DIFFRACTION EXPERIMENT, *AB INITIO* CALCULATIONS, CSD ANALYSIS AND MOLECULAR INTERACTION FIELD DETERMINATION

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New development in Structure-Based Drug Design (SBDD) is based on a better knowledge of interactions between drug (generally a small molecule) and the biological target (generally a protein) [1]. In that context, prediction and observation of interaction sites are crucial [2].
We have developed a combining approach mixing experimental determination and theoretical prediction. From high resolution X-ray diffraction experiment, electrostatic potential (EP) of drug could be determined. Experimental EP is directly comparable to theoretical EP determined through *ab initio* Gaussian calculations. EP localization indicates electrophile and nucleophile region. Precise analysis of crystallographic database (CSD, ICSD) can give a prediction of interaction site through the frequencies of non-covalent interactions as observed in the solid state. Finally, molecular interaction field determination obtained from GRID [3] a semi-empirical docking software is a fourth tool ; it gives for a small molecule, a prediction of the interaction site between the target (drug) and different probes (water, methyl, metal, aso…).
This approach will be explored on different drugs (busulfan [4a], paracetamol [4b], piracetam [4c]) or putative drug (salicylaldehyde thiosemicarbazone [4d], 4-methyl-3-thiosemicarbazide [4e], 4-Aryl-4-oxo-2-butenoic acids [4f]).
Development of this methodology will enhance interactions between medicinal chemists, biochemists and crystallographers.

[1] a) C. M. Henry. *Chem. Eng. News Archive*, (2001), 79, 69–78 ; b) A.T.R. Laurie, R. M. Jackson. *Current Protein and Peptide Science*, (2006), 7, 395-406
[2] M. Zurcher et al *J. Org. Chem.* (2008), 73, 4345–4361
[3] Goodford, P. J. A *J. Med. Chem.* 1985, 28, 849-857
[3] a) N. Ghermani et al, *Pharmaceutical Research*, (2004), 21, 598-607 ; b) N. Bouhmaida, *Acta Cryst*. (2009) B65, 363 ; c) MH Chambrier et al, *Cryst Growth & Design* (2011) 11 2528-2539 ; d) S. Novakovic et al, *Crystal Growth & Design*, (2007), 7, 191-195; e) B. Francuski, et al *CrystEngComm*, DOI: 10.1039/c0ce00760a ; f) Drakulic B., et al, *J. Med. Chem*, (2005), 48, 5600-5603

PREDVIĐANJE MESTA INTERAKCIJE KOD LEKOVA. KOMBINOVANI PRISTUP KOJI UKLJUČUJE RENDGENSKU DIFRAKCIJU VISOKE REZOLUCIJE, *AB INITIO* IZRAČUNAVANJE, CSD ANALIZU I ODREĐIVANJE INERAKCIONOG POLJA MOLEKULA

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Dizajniranje novih lekova na osnovu poznavanju struktura prethodnih ("Structure-Based Drug Design", SBDD) baziran je na razumevanju interakcija između leka (uglavnom malog molekula) i biološke mete (uglavnom protein) [1]. U tom kontekstu, predviđanje i posmatranje mesta interakcije je veoma značajno. [2].

Mi smo razvili kombinovani pristup koji uključuje eksperimentalno određivanje i teorijsko predviđanje. Elektrostatički potencijal (EP) molekula leka se može odrediti na osnovu podataka dobijenih rengenostrukturnom analizom visoke rezolucije. Eksperimentalno određeni EP može se direktno porediti sa teorijskim EP dobijenim *ab initio* izračunavanjem iz Gaussian-a. EP ukazuje na elektrofilne i nukleofilne oblasti molekula. Pored toga, detaljnom analizom kristalografskih baza (CSD, ICSD) možemo predvideti preferento mesto inetrakcije na osnovu učestalosti nekovalentnih interakcija posmatranih u čvrstom stanju. Određivanje polja interakcije molekula ("molecule interaction field" MIF) preko semi-empirijskog "docking" programa GRID [3], je četvrti način koji omogućava predviđanje mesta interakcije malog molekula (leka) sa različitim probama (voda, metil grupa, metal itd).

Ovakav pristup će se ispitivati na različitim lekovima (busulfan [4a], paracetamol [4b], piracetam [4c]) ili drugim potencijalno aktivnim molekulima (tiosemikarbazon salicilaldehida [4d], 4-metil-3-tiosemikarbazid [4e], 4-aril-4-okso-2-butenska kiselina [4f] itd). Razvojem ove metodologije poboljšaće se interakcija između medicinskih hemičara, biohemičara i kristalografa.

[1] a) C. M. Henry. *Chem. Eng. News Archive*, (2001), 79, 69–78 ; b) A.T.R. Laurie, R. M. Jackson. *Current Protein and Peptide Science*, (2006), 7, 395-406.
[2] M. Zurcher et al *J. Org. Chem.* (2008), 73, 4345–4361.
[3] Goodford, P. J. A *J. Med. Chem.* 1985, 28, 849-857.
[3] a) N. Ghermani et al, *Pharmaceutical Research*, (2004), 21, 598-607 ; b) N. Bouhmaida, *Acta Cryst.* (2009) B65, 363 ; c) MH Chambrier et al, *Cryst Growth & Design* (2011) 11 2528-2539 ; d) S. Novaković et al, *Crystal Growth & Design*, (2007), 7, 191-195; e) B. Francuski, et al *CrystEngComm*, DOI: 10.1039/c0ce00760a ; f) Drakulić B., et al, *J. Med. Chem*, (2005), 48, 5600-5603.

CRYSTAL STRUCTURE OF *O,O'*-DIPROPYL ESTER OF (*S,S*)-ETYLENEDIAMINE-*N,N'*-DI-2-(4-METHYL)--PENTANOIC ACID DIHYDROCHLORIDE

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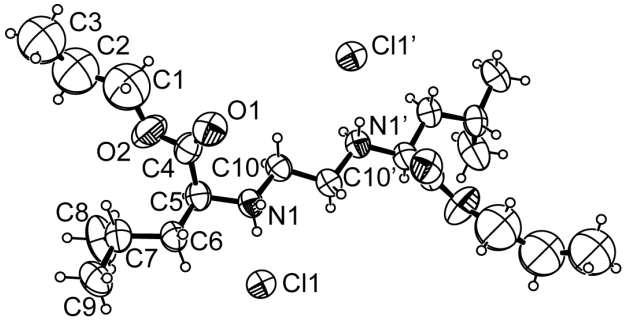
Bidentate *N,N'*-ligand precursor [1], *O,O'*-dipropyl ester of (*S,S*)--ethylenediamine-*N,N'*-di-2-(4-methyl)-pentanoic acid dihydrochloride, [(*S,S*)-H_2Pr_2eddl]Cl_2, was prepared and its crystal structure is given herein.

The ester was recrystallized from the warm propanol and after cooling at room temperature and standing for several days; crystals suitable for X-ray measurements were obtained. The diffraction data from a selected single crystal of [(*S,S*)-H_2Pr_2eddl]Cl_2 were collected at room temperature on Oxford Diffraction Xcalibur Gemini S diffractometer equipped with CuK_α radiation (λ = 1.54184 Å).

Crystallographic data: $C_{20}Cl_2H_{42}O_4N_2$, tetragonal crystal system, space group $P4_2$, a = 16.5620 (2) Å, b = 16.5620 (2) Å, c = 5.2240 (1) Å, V = 1432.9(3) Å^3, Z = 2, D_{calc} = 1.032 g cm^{-3}, μ = 2.215 mm^{-1}, F(000) = 484, crystal size 0.07 x 0.02 x 0.01 mm^3, R_{int} = 0.0663, R_1, wR_2 [I>2σ(I)] = 0.0769, 0.1911. The crystal packing is determined by strong intermolecular N−H...Cl and C−H…O hydrogen bonds.



[1] J. M. Vujić, M. Cvijović, G. N. Kaluđerović, M. Milovanović, B. B. Zmejkovski, V. Volarević, N. Arsenijević, T. J. Sabo, S. R. Trifunović, *Eur. J. Med. Chem.* **45** (2010) 3601.

KRISTALNA STRUKTURA *O,O'*-DIPROPIL ESTRA (*S,S*)-ETILENDIAMIN--*N,N'*-DI-2-(4-METIL)-PENTANSKE KISELINE DIHIDROHLORIDA

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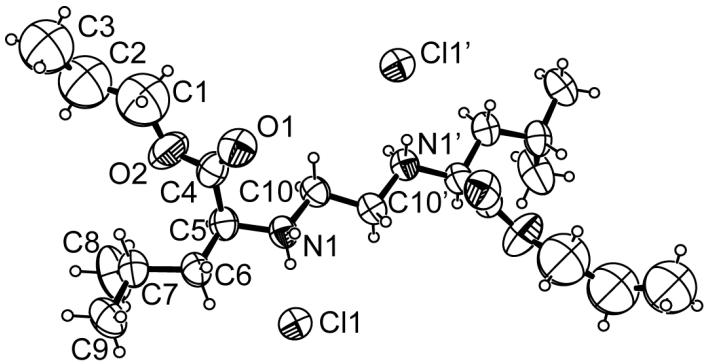
Sintetisan je bidentatni *N,N'* ligand prekursor [1], *O,O'*-dipropil estar (*S,S*)--etilendiamin-*N,N'*-di-2-(4-metil)-pentanske kiseline dihidrohlorida, [(*S,S*)-H_2Pr_2eddl]Cl_2 i ispitivana je njegova kristalna struktura. Estar je prekristalisan toplim propanolom i nakon nekoliko dana hlađenjem na sobnoj temperaturi, dobijeni su kristali pogodni za rendgensku strukturnu analizu. Difrakcioni podaci sa monokristala [(*S,S*)-H_2Pr_2eddl]Cl_2 prikupljeni su na sobnoj temperaturi na Oxford Diffraction Xcalibur Gemini S difraktometru opremljenim CuKα zračenjem (λ = 1,54184 Å).

Kristalografski podaci: $C_{20}Cl_2H_{42}O_4N_2$, tetragonalni kristalni sistem, prostorna grupa $P4_2$, a = 16,5620 (2) Å, b = 16,5620 (2) Å, c = 5,2240 (1) Å, V = 1432,9(3) Å^3, Z = 2, $D_{izrac.}$ = □1,032 g cm^{-3}, μ□□ = 2,215 mm^{-1}, F(000) = 484, veličina kristala 0,07 x 0,02 x 0,01 mm^3, R_{int} = 0,0663, R_1, wR_2 [I>2σ(I)] = 0,0769, 0,1911. Kristalno pakovanje određena je jakim intermolekulskim N−H...Cl i C−H…O vodoničnim vezama.



[1] J. M. Vujić, M. Cvijović, G. N. Kaluđerović, M. Milovanović, B. B. Zmejkovski, V. Volarević, N. Arsenijević, T. J. Sabo, S. R. Trifunović, *Eur. J. Med. Chem.* **45** (2010) 3601.