

СРПСКО КРИСТАЛОГРАФСКО ДРУШТВО

SERBIAN CRYSTALLOGRAPHIC SOCIETY

XV КОНФЕРЕНЦИЈА СРПСКОГ
КРИСТАЛОГРАФСКОГ ДРУШТВА

Изводи радова

XV CONFERENCE OF THE SERBIAN
CRYSTALLOGRAPHIC SOCIETY

Abstracts

КРАГУЈЕВАЦ – KRAGUJEVAC

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PLENARY LECTURES

PLENARNA PREDAVANJA

XAFS SPECTROSCOPIES AND CHEMISTRY: SOME SELECTED RESULTS

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XAFS spectroscopies extract structural information from a sample analysing its X-ray absorption spectrum. They allow us to determine the chemical environment of an element – in any aggregation state and under any kind of atmosphere – in terms of number and type of neighbours, interatomic distances and structural disorder. This determination is confined within a 4 – 8 Å radius from the element.

In this lecture the basic principles of XAFS spectroscopies will be briefly illustrated; at the same time experimental techniques and data analysis methods will be presented.

Finally some selected examples of application in chemistry will be discussed.

CRYSTAL CHEMISTRY OF ALKALINE EARTH OXO-ALUMINATES AND GALLATES

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The compounds belonging to the systems (Ca,Sr,Ba)O-Al₂O₃ occur in several technologically important processes. Pure calcium monoaluminate (CaAl₂O₄), for example, is the main phase in sulphate resistant calcium aluminate cements, comprising between 40-70 wt.% of the material [1]. Ca-, Sr- and Ba-aluminates of various compositions are used for the production of a new generation of persistent luminescence materials [2-5]. After doping with Eu²⁺ the aluminate phosphors show a strong, broad band blue/green emission characteristic. Furthermore, double oxides containing barium and aluminium are refractory, with several possible industrial uses [6].

In addition to investigations aimed on technological applications, calcium aluminates like CaAl₂O₄ have been also studied by earth scientists [7-9]. For instance, Akaogi et al. [9] examined the solid solution series (Mg_xCa_{1-x})Al₂O₄ at high pressures. They obtained a new so-called *hexagonal aluminous phase* and suggested that this compound could be one of the major constituent minerals in subducted basaltic crust in the upper part of the lower mantle. For the alkaline earth gallates only a few investigations aiming on technical applications have been performed so far. Poort et al. [10] studied their emission and absorption spectra after doping with europium, but the poor luminescence properties of the products as well as the comparatively high price for reagents containing gallium prevented the development of gallate based phosphors. However, from a crystal chemical point of view the comparison between aluminates and gallates of the same composition is extremely useful. Since Al and Ga belong to the same main group their double oxides can be used as perfect model systems to understand the influence of the cation radii on the observed structure types.

In contrast to the great number of investigations aimed to elucidate the phase equilibria in the systems (Ca,Sr,Ba)O-(Ga,Al)₂O₃ it is surprising that quite recently only a limited number of structural studies have been performed on these materials. In the course of our own research activities the following compounds have been structurally characterized for the first time (phases marked with *) have been prepared at elevated pressure):

<i>Compound</i>	<i>Structure types and/or building units</i>	
Ca ₂ (Al _x Ga _{1-x}) ₂ O ₅ (*)	Tetrahedra & octahedral	Ca ₄ Al ₆ O ₁₃ (*)
	Tetrahedra, trig. bipyramids, octahedral Sr ₃ Ga ₄ O ₉	
	Tetrahedral layers	
Ba ₄ Ga ₂ O ₇	Group gallate with Ga ₂ O ₇ -units	
Sr ₃ Ga ₂ O ₆		
Ba ₃ Ga ₂ O ₆		
Ba ₄ Al ₂ O ₇	Defect perovskites or structures with	
α-Sr ₁₀ Ga ₆ O ₁₉	X ₃ O ₁₀ , X ₆ O ₁₈ , X ₁₂ O ₃₆ , X ₆ O ₁₉ -groups	
β-Sr ₁₀ Ga ₆ O ₁₉		
Sr ₁₀ Al ₆ O ₁₉		
β-SrGa ₂ O ₄		
γ-SrGa ₂ O ₄ (*)		

α -BaGa₂O₄
 β -BaGa₂O₄
BaAlGaO₄

Tetrahedral frameworks

Although the chemistry of these compounds consisting of main group elements is not very extraordinary, it is interesting to note that a large variety of different structure types is covered. Most of the compounds are based on [AlO₄]- or [GaO₄]-tetrahedra with various degrees of connectivities. The structures of these materials are similar to those observed in silicates (which have been studied in much more detail) and can be classified using the same concepts proposed by Liebau [11]. However, many of the alkaline earth rich compounds can be related to the perovskite structure type as well. For example, the “cyclo-gallate” Sr₃Ga₂O₆ containing isolated six-membered [Ga₆O₁₈]-rings can be alternatively regarded as an example for a defect ABO₃-perovskite with 12.5% vacancies in the A-substructure and 25% oxygen vacancies: (Sr_{7/4}□_{1/4})(Ga_{3/4}Sr_{1/4})(O_{9/4}□_{1/4}).

Some preliminary studies have been performed to elucidate the influence of high pressure on the formation of novel phases. The experiments have shown that even at comparatively low pressures up to 2.5GPa new classes of compounds can be stabilized where unusual coordination environments for the trivalent cations could be realized. In the case of Ca₄Al₆O₁₃, for example, four-, five- and six-fold coordinated Al³⁺ has to be distinguished. The structure is build up from layers of perovskite-type corner-sharing [AlO₆]-octahedra linked by sheets containing tetrahedral zweier single chains as well as rods of trigonal bipyramids sharing common edges/corners.

Secondly, syntheses experiments in the system Ca₂(Al_xGa_{1-x})₂O₅ proved the existence of an isostructural solid solution series at elevated pressures. The compounds adopt the brownmillerite structure type, which can be classified as a defect perovskite as well. A third experiment conducted on SrGa₂O₄ resulted in the formation of a previously unknown modification, belonging to the so-called ABW zeolite structure type. Although more than 70 different structure determinations of compounds with ABW-type are known [12], the high pressure modification of SrGa₂O₄ is the only example where the tunnels within the tetrahedral framework are occupied by divalent cations.

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ORAL PRESENTATION

SAOPŠTENJA

SYNTHESIS AND CRYSTAL STRUCTURE OF 3 β -ACETOXY-17-BUTYL-17-OXO-16-NITRILE-16,17-SECO-5-ANDROSTENE

O. Klisurić^a, D. Lazar^a, S. Stanković^a, S. Stojanović^a, K. Penov-Gaši^a, M. Sakač^a, D. Zobel^b, A. Wagner^b

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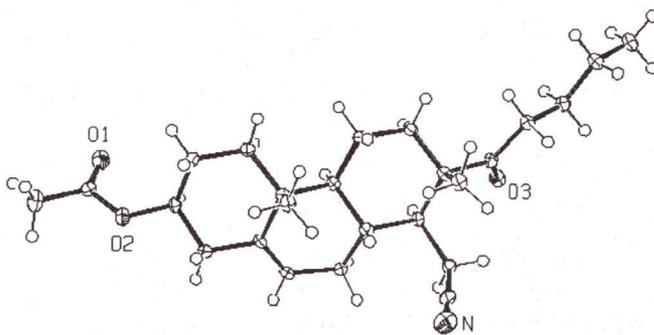
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In order to study androgenic vs. antiandrogenic activity, new compound, 3 β -acetoxy-17-butyl-17-oxo-16-nitrile-16,17-seco-5-androstene, was synthesized in several synthetic steps, starting from dehydroepiandrosterone.

The compound crystallizes in the monoclinic system, space group P2₁, with the unit cell parameters $a=11.724(3)$, $b=5.828(2)$, $c=16.932(4)$ Å, $\beta=105.151(7)$, $Z=2$, $D_x=0.59$ Mg m⁻³, $\mu=0.04$ mm⁻¹, MoK α radiation.

The crystal structure was solved by direct methods on the basis of 6085 independent reflections using SHELXS-97 [1] and refined by SHELXL-97 [1]. The final R factor is 0.052 for 4388 reflections with $I>4\sigma(I)$.



Perspective view of the molecule

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SINTEZA I KRISTALNA STRUKTURA 3 β -ACETOKSI-17-BUTIL-17-OKSO-16-NITRIL-16,17-SEKO-5-ANDROSTENA

O. Klisurić^a, D. Lazar^a, S. Stanković^a, S. Stojanović^a, K. Penov-Gaši^a, M. Sakač^a, D. Zobel^b, A. Wagner^b

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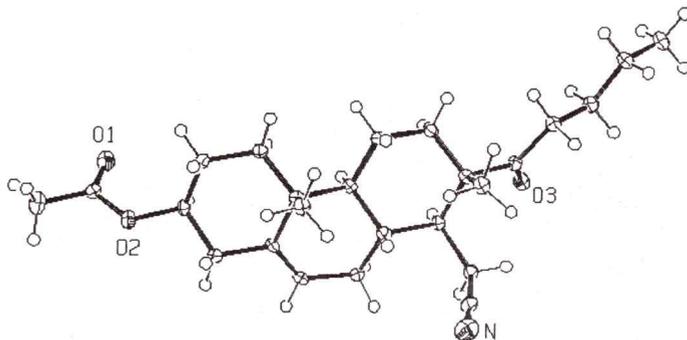
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U cilju ispitivanja androgene odnosno antiandrogene aktivnosti, polazeći od dehidroepiandrosterona, sintetizovano je, u više sintetskih faza, novo jedinjenje: 3 β -acetoxi-17-butil-17-okso-16-nitril-16,17-seko-5-androsten.

Jedinjenje kristališe u monokliničnom kristalografskom sistemu, prostorna grupa P2₁, sa parametrima elementarne ćelije a=11,724(3), b=5,828(2), c=16,932(4)Å, β =105,151(7), Z=2, D_x=0,59 Mg m⁻³, μ =0,04 mm⁻¹, MoK α zračenje.

Struktura kristala rešena je primenom direktnih metoda na bazi 6085 nezavisnih refleksa pomoću SHELXS-97 [1] i utačnjena pomoću SHELXL-97 [1]. Konačna vrednost R faktora je 0,052 za 4388 refleksa sa I>4 σ (I).



[1] G.M.Sheldrick, (1997) SHELX-97, *Program for the solution and trefinement of crystal structures*, University of Goettingen, Germany.

SYNTHESIS AND MOLECULAR STRUCTURE OF BINUCLEAR Ni(II)-Cu(II) COMPLEX CONTAINING ETHYLENEDIAMINE-DISUCCINATO LIGAND

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This communication presents a further step of our attempts directed to finding a structure relationship between copper(II) complexes that contain different hexadentate ligands of N₂O₄ chromophore [1]. The hexadentate H₄S,S-edds ligand (H₄S,S-edds stands ethylenediaminedisuccinic acid) has been prepared and used for preparation of corresponding mononuclear Ba[Cu(S,S-edds)] copper(II) complex. By chromatography techniques using strong acid cation exchange resin in Ni(II) form we prepared octahedral binuclear

Ni[Cu(S,S-edds)]x5H₂O complex (Figure 1) which has been characterized by IR and UV/Vis spectroscopy. The octahedral geometry of copper(II) complex has been verified by an X-ray structure analysis. The asymmetric unit contains one ionic dinuclear Ni-Cu complex (one formula unit with no atom setting at special position). Four water molecules are coordinated to Ni and the other two O-Ni bonds are from different symmetry related (-x, -1/2+y, 1/2-z) carboxylates of the ethylenediaminesuccinic acid ligands (O3 and O6), so forming an infinite helical type of chain along the base vector.

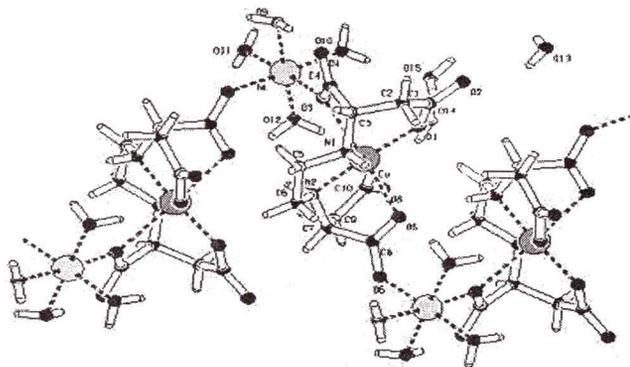


Figure 1. Molecular structure of Ni[Cu(S,S-edds)]x5H₂O

References

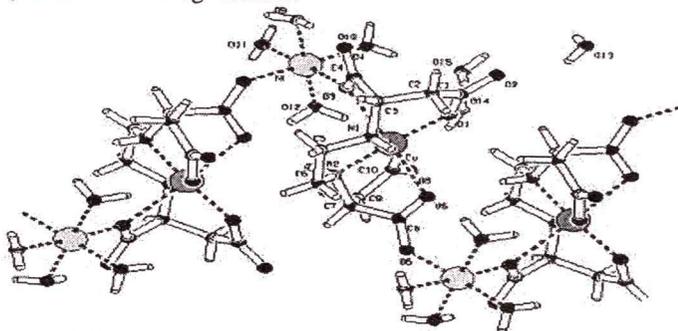
[1] D.J. Radanovi}, B.V. Prelesnik, D.D. Radanovi}, Z.D. Matovi} and B.E. Douglas, *Inorg. Chim. Acta*, **1997**, *262*, 203.

SINTEZA I MOLEKULSKA STRUKTURA BINUKLEARNOG Ni(II)-Cu(II) KOMPLEKSA KOJI SADRŽI ETILEN-DIAMIN-DISUKCINATO LIGAND

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Ovo saopštenje predstavlja dalji korak naših pokušaja usmerenih ka pronalaženju strukturnih odnosa između Cu(II) kompleksa koji sadrže različite heksadentatne ligande N₂O₄ hromofore [1]. U tu svrhu sintetisan je hexadentatni H₄S,S-edds ligand (H₄S,S-edds označava ethylendiamindisukcinatnu kiselinu) i iskorišćen za sintezu odgovarajućeg mononuklearnog Ba[Cu(S,S-edds)] kompleksa bakra. Hromatografskom tehnikom koristeći jako kiseli katjonski izmenjivač u Ni(II) obliku mi smo uspeli da nagradimo oktaedarski binuklearni Ni[Cu(S,S-edds)]x5H₂O complex (Slika 1) koji je karakterisan IR i UV/Vis spektroskopijom. Oktaedarska geometrija bakar(II) kompleksa verifikovana je X-ray strukturnom analizom. Asimetrična jedinica sadrži jedan jonski binuklearan Ni-Cu kompleks. Četiri molekula vode se nalaze koordinovana na nikel(II) jonu a preostale dve Ni-O veze potiču od različitih simetrijom odredjenih karboksilata (-x, -1/2+y, 1/2-z) etilendiaminsukcinato liganda (O3 i O6), formirajući na taj način beskonačan helikoidni tip lanca duž baznog vektora.



Slika 1. Molekulska struktura Ni[Cu(S,S-edds)]x⁵H₂O

Reference

- [1] D.J. Radanovi}, B.V. Prelesnik, D.D. Radanovi} Inorg. Chim. Acta, 1997, 262, 203.

THE CRYSTAL STRUCTURE OF ETHYLENEDIAMINE-N,N'-DI-S,S-2-PROPIONIC ACID MONOCHLORHYDRATE

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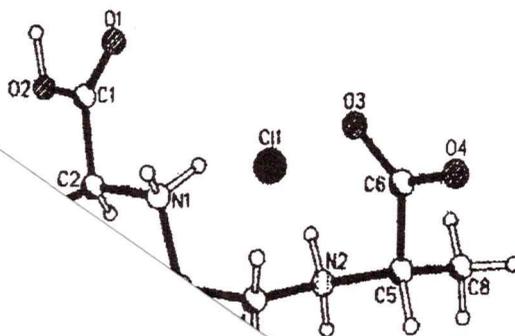
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Here we report the crystal data and the results of structure refinement of ethylenediamine-N,N'-di-S,S-2-propionic acid monochlorhydrate: $C_8H_{17}ClN_2O_4$, $M_r = 240.69$, triclinic crystal system, space group P1, crystal size $0.28 \times 0.22 \times 0.16$ mm, block shape and colorless, $a = 5.3902(2)$ Å, $b = 5.8967(2)$ Å, $c = 10.3319(2)$ Å, $\alpha = 99.625(2)^\circ$, $\beta = 91.645(2)^\circ$, $\gamma = 109.995(2)^\circ$, $V = 302.94(2)$ Å³, $Z = 1$, $F(000) = 128$, $\rho = 1.319$ g/cm³, the largest diff. peak and hole $(\Delta/\rho)_{\max} = 0.215$ and $(\Delta/\rho)_{\min} = -0.215$ eÅ⁻³, absorption coefficient μ (MoK α) = 0.314 mm⁻¹. Intensities of 2941 unique reflections are collected on a Bruker-Nonius Kappa CCD diffractometer [λ (MoK α) = 0.71073 Å] in range $7.4 \leq 2\theta \leq 58.0^\circ$.

The structure was solved and refined using program SHELXTL NT 6.12 with 8159 independent reflections up to $R = 3.18$ for 2941 observed reflections with $[I > 2\sigma(I)]$ $Rw_2 = 6.7\%$ (refinement on F^2) for all reflections and 205 refined parameters.



KRISTALNA STRUKTURA ETILENDIAMIN-N,N'-DI-S,S-2-PROPIONSKE KISELINE HLOORHIDRATA

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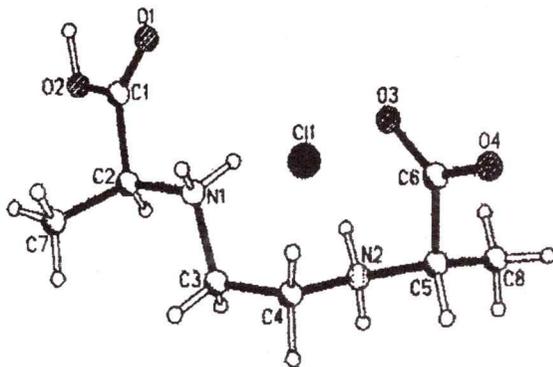
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Ovde su prikazani rezultati dobijeni rešavanjem kristalne strukture etilen-diamin-N,N'-di-S,S-2--propionske kiseline hlorhidrata: $C_8H_{17}ClN_2O_4$, $M_r = 240,69$, trikliničan kristalni sistem, prostorna grupa P1, veličina kristala $0,28 \times 0,22 \times 0,16$ mm, $a = 5,3902(2)$ Å, $b = 5,8967(2)$ Å, $c = 10,3319(2)$ Å, $\alpha = 99,625(2)^\circ$, $\beta = 91,645(2)^\circ$, $\gamma = 109,995(2)^\circ$, $V = 302,94(2)$ Å³, $Z = 1$, $F(000) = 128$, $\rho = 1,319$ g/cm³, $(\Delta\rho)_{\max} = 0,215$ and $(\Delta\rho)_{\min} = -0,215$ eÅ⁻³, μ (MoK α) = 0,314 mm⁻¹. Intenziteti 2941 pojedinačnih refleksija su izmereni pomoću Bruker-Nonius Kappa CCD difraktometra [λ (MoK α) = 0,71073 Å] u opsegu $7.4 \leq 2\theta \leq 58.0^\circ$.

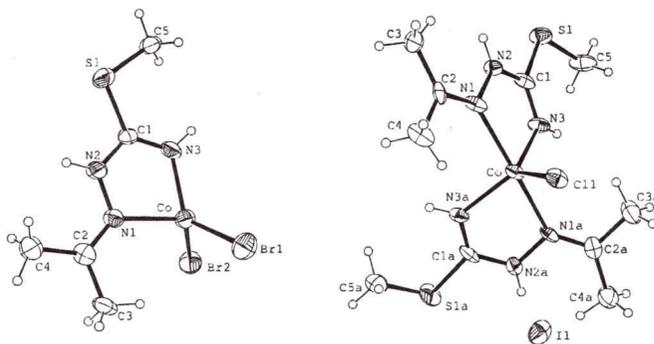
Struktura je rešena i utačnjena korišćenjem programa SHELXTL NT 6.12 na osnovu 8159 nezavisnih refleksija, do $R = 3,18\%$ za 2941 opaženu refleksiju [$I > 2\sigma(I)$] $Rw_2 = 6.7\%$ (utačnjavanje je vršeno pomoću F^2) za sve refleksije i 205 parametara.



CRYSTAL STRUCTURE OF TWO Co(II) COMPLEXES WITH ACETONE S-METHYLISOTHIOSEMICARBAZONE

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The tetrahedral complex $[\text{Co}(\text{L-ac})]\text{Br}_2$ was obtained in the reaction of the acetic solution of $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ and acetone S-methylisothiosemicarbazone (L-ac). The Co atom is placed in the center of a severely distorted tetrahedron with two Br atoms and two N atoms of the organic ligand in the apices. The angles involving the Co atom range from 80.3° to 119.2° and illustrate the distortion from the tetrahedral geometry.

Crystallographic data: $\text{C}_5\text{H}_{11}\text{Br}_2\text{CoN}_3\text{S}$, monoclinic crystal system, space group $\text{P}2_1/\text{n}$, $a = 8.065(15)$, $b = 10.875(10)$, $c = 13.039(8)$ Å, $\beta = 91.75(10)^\circ$, $V = 1143(2)$ Å³, $\mu(\text{MoK}\alpha) = 8.63$ mm⁻¹, Gaussian absorption correction, MoK α radiation, Enraf-Nonius CAD-4 diffractometer. The structure was solved using SHELXS86 and refined using SHELXL97 programs to the final R factor 9.1% for 934 reflections with $I > 2\sigma(I)$.

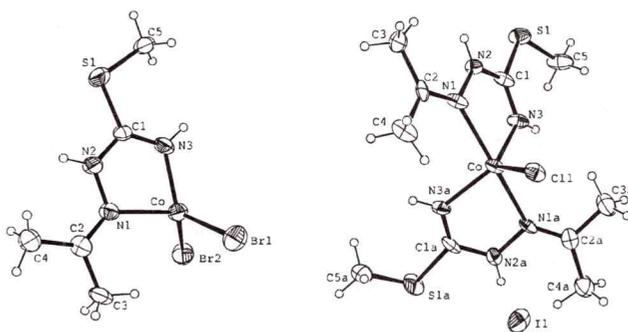
The trigonal-bipyramidal complex $[\text{Co}(\text{L-ac})_2\text{Cl}]\text{I}$ was obtained in the reaction of the methanolic solutions of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and methanol/acetone solution of S-methylisothiosemicarbazide hydrogeniodide in the presence of Na_2CO_3 . The equatorial part of the complex cation is formed by chlorine atom and two thioamide N atoms of the Schiff base while the hydrazine N atoms of the base occupy the apical sites. The calculated trigonality factor (τ) is 0.84 suggesting a considerable distortion of the trigonal-bipyramidal geometry.

Crystallographic data: $\text{C}_{10}\text{H}_{22}\text{ClCoIN}_6\text{S}_2$, monoclinic crystal system, space group $\text{P}2_1/\text{a}$, $a = 9.019(4)$, $b = 25.738(7)$, $c = 9.401(3)$ Å, $\beta = 117.15(2)^\circ$, $V = 1941.8(10)$ Å³, $\mu(\text{MoK}\alpha) = 2.83$ mm⁻¹, MoK α radiation, Enraf-Nonius CAD-4 diffractometer. The structure was solved using SHELXS86 and refined using SHELXL97 programs to the final R factor 8.0% for 1548 reflections with $I > 2\sigma(I)$.

KRISTALNA STRUKTURA DVA KOMPLEKSA Co(II) SA S-METILIZOTIOSEMIKARBAZONOM ACETONA

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Tetraedarski kompleks $[\text{Co}(\text{L-ac})]\text{Br}_2$ dobijen je u reakciji acetonskog rastvora $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ i S-metilizotiosemikarbazona acetona (L-ac). Atom Co nalazi se u centru deformisanog tetraedra na čijim se vrhovima nalaze dva atoma Br i dva N atoma organskog liganda. Uglovi koji uključuju Co atom kreću se u intervalu od 80.3° do 119.2° i ukazuju na značajnu deformaciju u tetraedarskoj geometriji kompleksa.

Kristalografski podaci: $\text{C}_5\text{H}_{11}\text{Br}_2\text{CoN}_3\text{S}$, monoklinični kristalni sistem, prostorna grupa $\text{P}2_1/\text{n}$, $a = 8,065(15)$, $b = 10,875(10)$, $c = 13,039(8)$ Å, $\beta = 91,75(10)^\circ$, $V = 1143(2)$ Å³, $\mu(\text{MoK}\alpha) = 8,63$ mm⁻¹, korekcija za absorpciju: Gausovska, MoK α zračenje, Enraf-Nonius CAD-4 difraktometar. Struktura je rešena pomoću programa SHELXS86 i utačnjena programom SHELXL97 do finalnog R-faktora od 9,1% za 934 refleksije sa $I > 2\sigma(I)$.

Trigonalno-bipiramidalni kompleks $[\text{Co}(\text{L-ac})_2\text{Cl}]\text{I}$ dobijen je u reakciji metanolnog rastvora $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ i metanolno-acetonskog rastvora S-metilizotiosemikarbazida hidrogen-jodida u prisustvu Na_2CO_3 . Ekvatorijalni deo kompleksnog katjona formiraju Cl atom i dva tioamidna N atoma Šifove baze dok hidrazinski N atomi baze zauzimaju apikalne pozicije. Izračunati faktor trigonalnosti (τ) iznosi 0.84 i ukazuje na značajnu deformaciju trigonalno bipiramidalne geometrije.

Kristalografski podaci: $\text{C}_{10}\text{H}_{22}\text{ClCoIN}_6\text{S}_2$, monoklinični kristalni sistem, prostorna grupa $\text{P}2_1/\text{a}$, $a = 9,019(4)$, $b = 25,738(7)$, $c = 9,401(3)$ Å, $\beta = 117,15(2)^\circ$, $V = 1941,8(10)$ Å³, $\mu(\text{MoK}\alpha) = 2,83$ mm⁻¹, MoK α zračenje, Enraf-Nonius CAD-4 difraktometar. Struktura je rešena na isti način kao i prethodna i utačnjena do konačnog R-faktora od 8,0% za 1548 refleksija sa $I > 2\sigma(I)$.

STUDY OF METAL LIGAND AROMATIC CATION - π INTERACTIONS OF AQUA COMPLEXES WITH PHENYL RING

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The cation- π interaction is recognized as an important noncovalent bonding force in a wide range of molecular systems. The gas-phase studies of ion molecule complexes established that cation binds strongly to simple aromatic systems. High-level theoretical studies of ion-molecule systems have shown excellent agreement between calculated and experimental bonding energies.

It was shown that cationic metal complex interacts strongly with the π systems of benzene, acetylene, and ethylene. Based on these calculations, we proposed that cation- π interactions might exist when ligands coordinated to metal can get in contact with π system. It can be the case in metalloproteins, in metal complexes, in supramolecular structures, and when DNA and RNA interact with metal cations [1,2].

Because it was shown that MLAC- π interactions can exist in many molecular systems, it is interesting to find out details about the geometry of these cation- π systems; distances and mutual orientations of metal complex and phenyl ring. In this work, we screened crystal structures of metal complexes in Cambridge Structural Database (CSD) in order to find structures in which one or more water molecules coordinated to a transition metal cation interacts with aromatic system.

Screening the CSD provided over 100 structures in which an aromatic ring is close to a metal. We inspected these structures and selected 20 structures where the O... π_c (π_c – center of the phenyl ring) distances were very short, and at the same time the O-H... π_c angle was around 180°. These data indicates that there is a very strong MLAC- π interaction between water ligand and aromatic system. By quantum chemical calculations we evaluated bonding energies between $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ complex cation and benzene molecule

[1] S. D. Zaric; *Eur. J. Inorg. Chem.*, (2003), 2197.

[2] M. K. Milcic, Z. D. Tomic, S. D. Zaric, *Inorg. Chim. Acta*, article in press

PROUČAVANJE METAL LIGAND AROMATSKIH KATJON- π INTERAKCIJA AKVA KOMPLEKSA SA FENILNOM GRUPOM

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Katjon- π interakcije su veoma važne nekovalentne vezivne interakcije u mnogim molekularnim sistemima. Proučavanja na jon molekularnim kompleksima u gasnoj fazi utvrdila su da se katjon čvrsto vezuje za proste aromatične sisteme. Teorijska izučavanja najnovije generacije na jon molekularnim kompleksima pokazala su odlično slaganje između izračunatih i eksperimentalno određenih vezivnih energija.

Takodje je pokazano da katjonski metalni kompleksi snažno interaguju sa π sistemima benzena, acetilena i etilena. Na osnovu ovih proračuna, predloženo je da katjon- π interakcije mogu postojati kada ligandi koordinovani za metal mogu stupiti u kontakt sa π sistemom. Takve interakcije su opažene u metaloproteinima, kompleksima prelaznih metala, supramolekularnim strukturama i u slu-ajevima kada DNK i RNK interaguju sa katjonima metala [1,2].

Zbog postojanja MLAC- π interakcija u mnogim molekularnim sistemima potrebno je saznati što više detalja o geometriji tih katjon- π sistema, kao i rastojanja i međusobne orijentacije kompleksa prelaznog metala i fenil grupe. U ovom radu pretražili smo kristalne strukture metalnih kompleksa iz Kembridžske banke kristalografskih podataka (CSD) da bi pronašli strukture u kojima jedan ili više molekula vode, koji se nalaze koordinovani za katjon prelaznog metala, interaguju sa aromatičnim sistemom.

Pretraživanjem banke kristalografskih podataka pronašli smo preko 100 struktura u kojima je aromatični prsten blizu metala. Sve te strukture smo pregledali i izabrali 20 struktura u kojima je $O \cdots \pi_c$ (π_c – centar fenilnog prstena) rastojanje bilo kratko a u isto vreme $O-H \cdots \pi_c$ ugao je iznosio oko 180° . Ovi podaci ukazuju na postojanje veoma jakih MLAC- π interakcija između molekula vode koordinovanog za katjon prelaznog metala i aromatičnog sistema. Kvantno hemijskim proračunima odredili smo vezivnu energiju između $[Co(H_2O)_6]^{3+}$ kompleksnog katjona i molekula benzena

[1] S. D. Zarić; *Eur. J. Inorg. Chem.*, (2003), 2197.

[2] M. K. Milčić, Z. D. Tomić, S. D. Zarić, *Inorg. Chim. Acta*, article in press.

CRYSTALLOGRAPHICAL DATA FOR ARAGONITES FROM THE LOWER-MEOTIAN LAMINITES AT DJERDAP II

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In the framework of investigations of the white and gray laminas from the Lower-Meotian laminites at Djerdap II locality, it was established that they are composed from aragonite, Mg-calcite, quartz, feldspats and clay minerals [1].

On this occasion these aragonites are in detail crystallographically investigated and compared with the literature data [2].

The results are presented in Tables 1 and 2.

Table 1: Values for the hkl and d of aragonites

Keller et al.		white laminas			grey laminas		Keller et al.		white laminas			grey laminas	
h k l	d _{obs}	d _{calc}	d _{obs}	d _{calc}	d _{obs}	h k l	d _{obs}	d _{calc}	d _{obs}	d _{calc}	d _{obs}	d _{calc}	d _{obs}
1 1 0	4.2120	4.2087	4.2000	/	/	2 0 2	1.8775	1.8759	1.8754	/	/		
0 2 0	3.9840	3.9800	3.9682	/	/	1 3 2	1.8149	1.8131	1.8134	1.8135	1.8146		
1 1 1	3.3970	3.3937	3.3876	3.3955	3.3914	1 4 1	1.7598	1.7580	1.7591	1.7574	1.7580		
0 2 1	3.2740	3.2703	3.2657	3.2701	3.2710	1 1 3	1.7430	1.7412	1.7421	1.7431	1.7431		
0 0 2	2.8720	2.8689	2.8701	/	/	2 3 1	1.7290	1.7275	1.7278	/	/		
1 2 1	2.7330	2.7300	2.7277	/	/	0 2 3	1.7257	/	/	1.7254	1.7263		
0 1 2	2.7020	2.6990	2.6985	2.7017	2.7021	2 2 2	1.6984	1.6968	1.6972	/	/		
2 0 0	2.4810	2.4793	2.4773	2.4805	2.4799	0 4 2	1.6369	1.6351	1.6336	1.6351	1.6330		
0 3 1	2.4110	2.4083	2.4080	2.4075	2.4065	3 1 0	1.6198	1.6183	1.6187	/	/		
1 1 2	2.3730	2.3706	2.3701	2.3727	2.3716	3 1 1	1.5588	1.5576	1.5578	1.5583	1.5587		
1 3 0	2.3420	2.3395	2.3386	2.3385	2.3398	0 5 1	1.5357	1.5341	1.5346	/	/		
2 1 1	2.1900	2.1882	2.1874	2.1893	2.1897	2 4 1	1.4993	1.4981	1.4985	1.4979	1.4987		
2 2 0	2.1080	2.1044	2.1035	2.1047	2.1042	3 2 1	1.4764	1.4751	1.4756	1.4757	1.4751		
2 2 1	1.9774	1.9757	1.9754	1.9763	1.9764	1 5 1	1.4672	1.4655	1.4660	1.4649	1.4651		
0 4 1	1.8821	1.8801	1.8805	1.8793	1.8787								

Table 2: Calculated unit cell dimensions of aragonites

	Keller et al.	white laminas	grey laminas
a ₀ (Å)	4.9623	4.958(1)	4.961(1)
b ₀ (Å)	7.968	7.960(2)	7.955(2)
c ₀ (Å)	5.7439	5.738(2)	5.745(2)
V ₀ (Å ³)	227.11	226.47(8)	226.71(9)

Obtained data indicate that Ca²⁺ ions are not exchanged with Sr²⁺, Pb²⁺ and/or Ba²⁺ as usually, but with ions of smaller ionic radius (e.g. Mg²⁺).

[1] Petrovic, S. i Tancic, P. (1998): XIII Kongres Geologa Jugoslavije, II, 41-45, Herceg Novi.

[2] Keller, L., Rask, J. and Buseck, P., (1989): JCPDS 41-1475, Aragonite, Arizona State Univ., Tempe, AZ, USA, ICDD Grant-In-Aid.

KRISTALOGRAFSKI PODACI ZA ARAGONITE IZ DONJE-MEOTSKIH LAMINITA DJERDAPA II

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U okviru ispitivanja belih i sivih lamina iz donje-meotskih laminita na lokalitetu Djerdap II, utvrđeno je da se sastoje od aragonita, Mg-kalcita, kvarca, feldspata i glinovitih minerala [1].

Ovom prilikom su ovi aragoniti detaljnije kristalografski ispitani i upoređeni sa podacima iz literature [2].

Rezultati su prikazani u Tabelama 1 i 2.

Tabela 1: Vrednosti za hkl i d aragonita

Keller i dr.		bele lamine			sive lamine			Keller i dr.		bele lamine			sive lamine		
h k l	d _{izm}	d _{izr}	d _{izm}	d _{izr}	d _{izm}	h k l	d _{izm}	d _{izr}	d _{izm}						
110	4,2120	4,2087	4,2000	/	/	202	1,8775	1,8759	1,8754	/	/				
020	3,9840	3,9800	3,9682	/	/	132	1,8149	1,8131	1,8134	1,8135	1,8146				
111	3,3970	3,3937	3,3876	3,3955	3,3914	141	1,7598	1,7580	1,7591	1,7574	1,7580				
021	3,2740	3,2703	3,2657	3,2701	3,2710	113	1,7430	1,7412	1,7421	1,7431	1,7431				
002	2,8720	2,8689	2,8701	/	/	231	1,7290	1,7275	1,7278	/	/				
121	2,7330	2,7300	2,7277	/	/	023	1,7257	/	/	1,7254	1,7263				
012	2,7020	2,6990	2,6985	2,7017	2,7021	222	1,6984	1,6968	1,6972	/	/				
200	2,4810	2,4793	2,4773	2,4805	2,4799	042	1,6369	1,6351	1,6336	1,6351	1,6330				
031	2,4110	2,4083	2,4080	2,4075	2,4065	310	1,6198	1,6183	1,6187	/	/				
112	2,3730	2,3706	2,3701	2,3727	2,3716	311	1,5588	1,5576	1,5578	1,5583	1,5587				
130	2,3420	2,3395	2,3386	2,3385	2,3398	051	1,5357	1,5341	1,5346	/	/				
211	2,1900	2,1882	2,1874	2,1893	2,1897	241	1,4993	1,4981	1,4985	1,4979	1,4987				
220	2,1080	2,1044	2,1035	2,1047	2,1042	321	1,4764	1,4751	1,4756	1,4757	1,4751				
221	1,9774	1,9757	1,9754	1,9763	1,9764	151	1,4672	1,4655	1,4660	1,4649	1,4651				
041	1,8821	1,8801	1,8805	1,8793	1,8787										

Tabela 2: Izračunate dimenzije jediničnih ćelija aragonita

	Keller i dr.	bele lamine	sive lamine
a ₀ (Å)	4,9623	4,958(1)	4,961(1)
b ₀ (Å)	7,968	7,960(2)	7,955(2)
c ₀ (Å)	5,7439	5,738(2)	5,745(2)
V ₀ (Å ³)	227,11	226,47(8)	226,71(9)

Dobijeni podaci ukazuju da Ca²⁺ joni nisu zamenjeni sa Sr²⁺, Pb²⁺ i/ili Ba²⁺ kao što je uobičajeno, već sa jonima manjeg jonskog radijusa (npr. Mg²⁺).

[1] Petrović, S. i Tančić, P. (1998): XIII Kongres Geologa Jugoslavije, II, 41-45, Herceg Novi.

[2] Keller, L., Rask, J. and Buseck, P., (1989): JCPDS 41-1475, Aragonite, Arizona State Univ., Tempe, AZ, USA, ICDD Grant-In-Aid.

ABOUT DIFFERENT AFFINITIES OF METAL ATOMS TOWARD PHENYL RING

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The detailed knowledge of coordination sphere around metal atom is important for consideration of their various properties, including spectral and magnetic behavior. The role of weakly coordinated ligands in that sense is particularly difficult to determine due to small energy of interaction. The notion that metal-phenyl contacts can be explained in terms of interaction between the two species has attracted much attention due to their role in biological systems. It was also observed that interaction between the copper and phenyl carbon could serve as a path for magnetic interaction.

In a recent article [1] we have shown that intermolecular contacts between the copper and phenyl carbon are influenced by the presence of the chelate ring. If copper atom is part of the chelate ring, the distance between the copper and closest aromatic carbon is less than the sum of the respective van der Waals radius. In the absence of chelate ring the same distance is in almost all cases greater than the sum of van der Waals radius. This observation, and other geometric properties of copper-phenyl carbon contacts, has been explained in terms of stacking interaction between the chelate and phenyl rings. In this work we have applied the same approach, but include all metal atoms in the analysis, by using data stored in Cambridge Data Base. Only the Pd, Pt, Ni, Cu, Rh, Au, Zn, Ir and Co atoms are present in enough number of structures, to allow statistically correct conclusions. The results show that these metals show markedly different behavior, *ie.* the copper is unique in that sense. The factors that could possibly be responsible for this difference will be discussed.

[1] Z. D. Tomić, S. B. Novaković, S. D. Zarić, Eur. J. Inorg. Chem., (2004), 2215-2218

О РАЗЛИЧИТОЈ СКЛОНОСТИ МЕТАЛНИХ АТОМА КА ОСТВАРИВАЊУ ИНТЕРАКЦИЈЕ СА ФЕНИЛНИМ ПРСТЕНОМ

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За разумевање различитих својстава металних атома у комплексним једињењима неопходно је што потпуније познавање њихове координационе сфере. У том смислу је, због мале енергије интеракције, посебно тешко утврдити какав је утицај слабо координованих лигананда. Један од таквих примера је интеракција између атома метала и фенилног прстена, која се доста проучава због могуће важности за тумачење својстава биолошких система. Такође је опажено да интеракција између атома бакра и угљеника из фенилног прстена може да има улогу путање за магнетну интеракцију.

У недавно објављеном раду [1] показано је да на контакт између атома бакра и фенилног прстена утиче присуство хелатног прстена. Наиме, уколико је атом бакра део хелатног прстена, растојање бакар-фенилни угљеник тежи вредности мањој од збира одговарајућих ван дер Валсових полупречника, док је у одсуству хелатног прстена ово растојање значајно дуже. То опажање, као и остала геометријска својства овог контакта, је протумачено као последица интеракције између хелатног и фенилног прстена. У овом раду смо исти приступ применили на пручавање склоности других метала ка остваривању блиског контакта са фенилним прстеном. Коришћени су подаци који се налазе у Кристалографској бази података у Кембриџу. Овакав приступ је било могуће применити само за атоме Pd, Pt, Ni, Cu, Rh, Au, Zn, Ir и Co, јер се једино они налазе у довољном броју структура да би закључци били у складу са статистичким критеријумима који се примењују у оваквим анализама. Резултати показују да у поређењу са бакром, ови метали показују битно различито понашање у смислу склоности ка формирању блиских контаката са фенилним прстеном.

У овом раду ћемо изложити нека опажања везана за могуће чиниоце који доводе до опажене разлике.

[1] З. Д. Томић, С. Б. Новаковић, С. Д. Зарић, *Eur. J. Inorg. Chem.*, (2004), 2215-2218

A METHOD FOR OBTAINING CRYSTALS IN A TUBE FURNACE

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Analysis of a series of methods for obtaining crystals from melts showed that Tamman's method can be applied in a laboratory tube furnace [1]. The original apparatus we have constructed, based on Tamman's method, is schematically given in figure 1. It enables regulation and simultaneous crystallization of several substances, with several different: crystal nucleations, temperature gradients and crystallization rates.

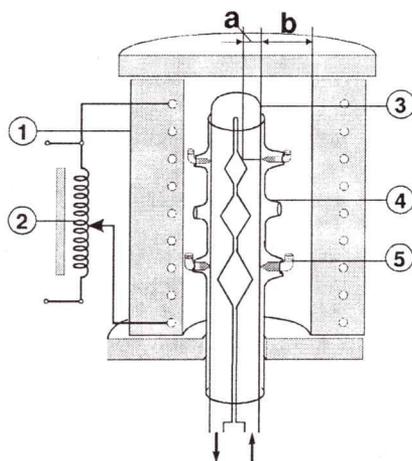


Figure 1. Apparatus for obtaining crystals: (1) laboratory tube furnace, (2) continuously changeable transformer, (3) air cooler ("cold tree"), (4) movable cylindrical tube with the mounting holes ("test sieve") and (5) family of ("grafted") Tamman's test tubes.

The crystallization rate in each of Tamman's test tube is regulated by the cross-section of the air flow (a), i.e. by the position of its point touching the cooler. Temperature gradients are regulated by the distance between the cooler and furnace wall (b). This method can also be applied in a crucible furnace [2].

[1] K.-Th.Wilke, J. Bohm, *Kristallzüchtung*, Deutscher Verlag der Wissenschaften, Berlin (1988), 591-608.

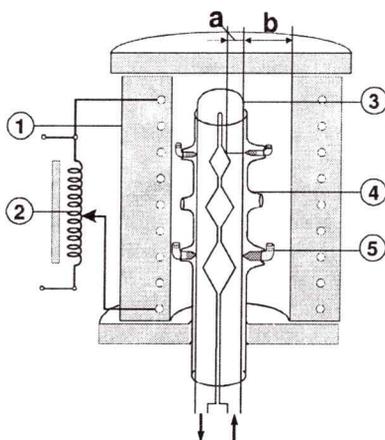
[2] B. Čabrić, T. Pavlović, A. Janićijević, *J. Cryst. Growth*, **200** (1999), 339-340.

МЕТОДА ЗА ДОБИЈАЊЕ КРИСТАЛА У ЦИЛИНДРИЧНОЈ ПЕЋИ

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Од низа метода за добијање монокристала из растопа, нашли смо да се у лабораторијској цилиндричној пећи може применити Таманова (G. Tamman) метода [1]. Оригинална апаратура коју смо конструисали на, основу Таманове методе, шематски је приказана на слици 1. Она омогућава регулацију и симултану кристализацију неколико субстанци, са неколико различитих: зачећа, температурских градијената и брзина кристализација.



Слика 1. Апаратура за добијање кристала: (1) лабораторијска цилиндрична пећ, (2) континуално променљиви трансформатор, (3) ваздушни хладњак («хладано дрво»), (4) помична цилиндрична цев са рупицама («пробно сито») и (5) фамилија («накалемљених») Таманових епрувета.

Брзина кристализације у свакој Тамановој епрувети се регулише помоћу попречног пресека ваздушне струје (а) тј. положаја њеног додира са хладњаком. Температурски градијенти се регулишу помоћу растојања хладњака од зида пећи (b). Ова метода може се применити и у тигл пећи [2].

[1] К.-Th. Wilke, J. Bohm, *Kristallzüchtung*, Deutscher Verlag der Wissenschaften, Berlin (1988), 591-608

[2] Б. Чабрић, Т. Павловић, А. Јанићијевић, *J. Cryst. Growth*, **200** (1999), 339-340

COMPARATIVE STUDY OF INTERMOLECULAR C–H... π INTERACTIONS IN METAL-PORPHYRIN COMPLEXES

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Weak hydrogen bonds and especially C–H... π interactions have been studied very intensively [1]. These interactions are of fundamental importance in structural chemistry and biology, supramolecular chemistry and crystal engineering because of their role in the molecular association and intermolecular interactions.

We noticed [2] that six-membered chelate rings with delocalized π bonds can be involved in C–H... π interactions as a π system. After that we analyzed C–H... π interactions in metal-porphyrin complexes. Namely, porphyrine and derivatives of porphyrine are coordinated to the metal atoms as tetradentate ligands forming four six-membered chelate rings. These rings possess π system able to participate in inter- and intramolecular C–H... π interactions which were studied in our recent papers [3,4]. In present work we will present the results of comparative study based on the data retrieved from the Cambridge Structural Database (CSD). Ring centroids for all pyrrole (C/C/C/C/N) and chelate (M/N/C/C/C/N) rings as well as other relevant points (centers of atoms and midpoints of C–C and N–C bonds) have been tested on the presence of C–H... π interactions. The data for all significant points have been compared giving unambiguous conclusion that preferential points for intermolecular C–H... π interactions in porphyrine skeleton are centroids of pyrrole and chelate rings.

[1] G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bonds in Structural Chemistry and Biology*, Oxford University Press, 1999.

[2] G. A. Bogdanović, A. Spasojević-de Bire, S. D. Zarić, *Eur. J. Inorg. Chem.* (2002) 1599.

[3] G. A. Bogdanović, V. Medaković, M. K. Miličić, S. D. Zarić, *Int. J. Mol. Sci.* (2004) 174.

[4] V. Medaković, M. K. Miličić, G. A. Bogdanović, S. D. Zarić, accepted in *J. Inorg. Biochem.*

KOMPARATIVNA STUDIJA INTERMOLEKULSKIH C–H... π INTERAKCIJA U METAL-PORFIRIN KOMPLEKSIMA

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Slabe vodonične veze a posebno C–H... π interakcije veoma su obimno istraživane [1]. Ove interakcije su od fundamentalnog značaja u strukturnoj hemiji i biologiji, supramolekularnoj hemiji i kristalnom inženjeringu zbog njihove uloge u udruživanju molekula i intermolekulskim interakcijama.

Mi smo opazili [2] da šestočlani helatni prstenovi sa delokalizovanim π vezama takođe mogu učestvovati u C–H... π interakcijama i to kao π sistem. Nakon toga smo analizirali C–H... π interakcije u metal-porfirin kompleksima. Naime, porfirini i njihovi derivati se koordinuju na atome metala kao tetradentatni ligandi uz formiranje četiri šestočlana helatna prstena. Ovi prstenovi poseduju π sistem sposoban da učestvuje u inter- i intramolekulskim C–H... π interakcijama što je i bilo predmet proučavanja u našim skorašnjim radovima [3,4]. U ovom radu mi ćemo predstaviti rezultate komparativne studije zasnovane na podacima o kristalnim strukturama iz relevantne baze podataka - Cambridge Structural Database. Na prisustvo C–H... π interakcija testirani su centri svih pirolnih (C/C/C/C/N) i helatnih (M/N/C/C/C/N) prstenova kao i druge relevantne tačke (atomi i sredine C–C i C–N veza). Podaci za sve značajne tačke u porfirinu su međusobno upoređene dajući nedvosmislen zaključak da su centri pirolnih i helatnih prstenova preferentne tačke za građenje intermolekulskih C–H... π interakcija kod metal-porfirin kompleksa.

[1] G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bonds in Structural Chemistry and Biology*, Oxford University Press, **1999**.

[2] G. A. Bogdanović, A. Spasojević-de Bire, S. D. Zarić, *Eur. J. Inorg. Chem.* (**2002**) 1599.

[3] G. A. Bogdanović, V. Medaković, M. K. Miličić, S. D. Zarić, *Int. J. Mol. Sci.* (**2004**) 174.

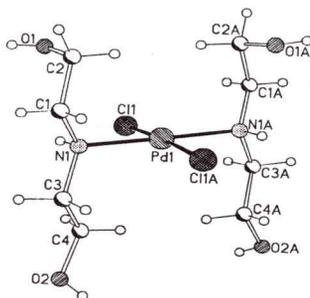
[4] V. Medaković, M. K. Miličić, G. A. Bogdanović, S. D. Zarić, accepted in *J. Inorg. Biochem.*

THE CRYSTAL STRUCTURE OF *trans*-[PdCl₂(DEAM)₂]

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The complex [PdCl₂(DEAM)₂], where DEAM = diethanolamine, was synthesized according to the modified procedure published in the literature [1]. This yellow-orange crystals of complex were undergone to elemental microanalysis and X-ray crystallography.



The experimental results of the elemental analysis for C, N and H are in accordance with calculated (Found (%): C, 24,93; N, 7,203; H, 5,646. Calc.: C, 24,77; N, 7,22; H, 5,68).

The crystal structure of our complex was solved and refined using program SHELXTL NT 6. 12

Crystal data: empirical formula C₈H₂₂Cl₂N₂O₄Pd and M_r = 387.58, tetragonal system, space group P4(2)bc, unit cell dimensions: a = 9.835(1) Å, b = 9.835(1) Å, c = 14.328(2) Å, α = β = γ = 90°, V = 1385.9(3) Å³, Z = 4, F(000) = 784, ρ_x = 1.858 g/cm³, μ(MoKα) = 1.729 mm⁻¹, 20852 independent reflections R = 5.9% for 1792 observed reflections with I > 2σ(I), R_w = 4.29% (refinement on F²) for all reflections and 111 refined parameters, (Δρ)_{max} = 0.433eÅ⁻³, (Δρ)_{max} = - 0.359eÅ⁻³, GOOF = 1.016

[1] H. Hohman, R. Van Eldik, *Inorg. Chim. Acta*, **174** (1990), 87

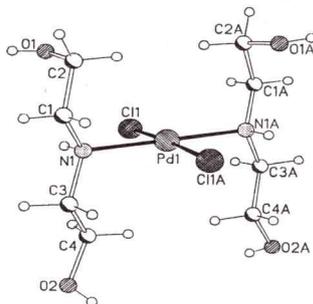
KRISTALNA STRUKTURA *trans*-[PdCl₂(DEAM)₂]

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Kompleks [PdCl₂(DEAM)₂], gde je DEAM = dietanolamin, je sintetizovan po modifikovanom postupku koji je ranije opisan u literaturi [1]. Ovaj žuto-narandžasti kristal kompleksa je podvrgnut elementarnoj mikroanalizi i rendgenskoj strukturnoj analizi.



Eksperimentalni rezultati elementarne mikroanalize za C, N i H su u saglasnosti sa teorijski izračunatim vrednostima (Nadjeno (%): C, 24,93; N, 7,203; H, 5,646. Izračunato: C, 24,77; N, 7,22; H, 5,68%).

Kristalna struktura našeg kompleksa je rešena i utačnjena korišćenjem programa SHELXTL NT 6.12.

Kristalografski podaci: C₈H₂₂Cl₂N₂O₄Pd, Mr = 387,58, tetragonalni kristalni sistem, prostorna grupa P4(2)bc, parametri elementarne ćelije kristala: a = 9,835(1) Å, b = 9,835(1) Å, c = 14,328(2) Å, α = β = γ = 90°, V = 1385,9(3) Å³, μ(MoKα) = 1,729 mm⁻¹, Z = 4, ρ_x = 1,858 g cm⁻³, F(000) = 784, 20852 nezavisne refleksije R = 5,9% za 1792 opaženih refleksija sa I > 2σ(I), R_{w2} = 4,29% (utačnjavanje pomoću F²) za sve refleksije i 111 utačnjenih parametara sa Δρ_{max} = 0,433, Δρ_{min} = -0,359 eÅ⁻³, GOOF = 1,016.

[1] H. Hohman, R. Van Eldik, *Inorg. Chim. Acta*, **174** (1990), 87

A NOVEL BINUCLEAR COBALT(II) PYROMELLITATO COMPLEX: HEXAAQUA-BIS(2,2'-BIPYRIDINE)- μ -(1,2,4,5- BENZENETETRACARBOXYLATO)DICOBALT(II) DIHYDRATE

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The coordination chemistry of pyromellitato, pyr (1,2,4,5-benzene-tetracarboxylato), transition metal complexes has received considerable attention owing to the variety of bridging abilities of pyr in the formation of mixed ligand compounds.

The title compound, $[\text{Co}_2(\text{pyr})(\text{bipy})_2(\text{H}_2\text{O})_6]\cdot 2\text{H}_2\text{O}$, (bipy = 2,2'-bipyridine), is a novel example of mixed ligand binuclear complex, where pyr is bis-monodentately coordinated, while the other two COO groups are not coordinated, but they are involved in the network of hydrogen bonds. Thus, each pyr is a bridging ligand linking two metal centres and forming binuclear units, with bipy ligands *trans* to each other. The Co(II) atom is in the deformed octahedral environment with the bond distances and the angles in the range of 2.071(2) – 2.174(2) Å and 76.21(8) – 97.10(7)°, respectively.

Crystal data: $[\text{Co}_2(\text{pyr})(\text{bipy})_2(\text{H}_2\text{O})_6]\cdot 2\text{H}_2\text{O}$, $\text{C}_{30}\text{H}_{34}\text{Co}_2\text{N}_4\text{O}_{16}$, $M_r = 824.48$, monoclinic, space group $P2_1/n$, $a = 12.516(3)$, $b = 7.589(2)$, $c = 17.907(5)$ Å, $\beta = 100.02(2)$ °, $V = 1674.9(8)$ Å³, $Z = 2$, $F(000) = 848$, $\rho_x = 1.635$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 1.073$ mm⁻¹, 3205 independent reflections, $R_1 = 3.08$ % for 2807 observed reflections with $I > 2\sigma(I)$, $R_{w2} = 7.98$ % for all reflections and 235 refined parameters.

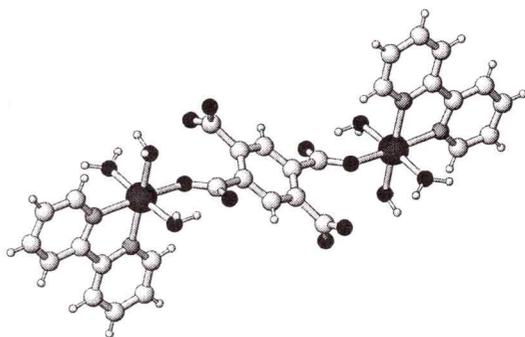


Figure. View of the binuclear unit.
Slika. Prikaz binuklearne jedinice.

NOVI BINUKLEARNI KOBALT(II) PIROMELITATO KOMPLEKS: HEKSAAKVA-BIS(2,2'-BIPIRIDIN)- μ -(1,2,4,5- BENZENTETRAKARBOKSILATO)DIKOBALT(II)-DIHIDRAT

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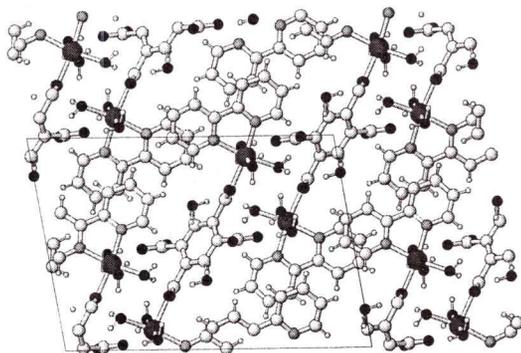
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Koordinaciona hemija piromelitato, pyr (1,2,4,5-benzentetrakarboksilato), kompleksa prelaznih metala privukla je značajnu pažnju zbog mnoštva mogućnosti mostovne koordinacije pyr-jona.

Opisano jedinjenje, $[\text{Co}_2(\text{pyr})(\text{bipy})_2(\text{H}_2\text{O})_6]\cdot 2\text{H}_2\text{O}$, (bipy = 2,2'-bipiridin), je novi primer mešovitog, binuklearnog kompleksa u kojem je pyr bis-monodentatno koordiniran, dok su druge dve COO grupe nekoordinirane, ali učestvuju u mreži vodoničnih veza. Stoga je svaki pyr-jon mostovni ligand koji povezuje dva metalna centra i formira binuklearne jedinice sa bipy ligandima u *trans* položaju. Co(II) atom je u deformisano-oktaedarskom okruženju sa dužinama veza i uglovima u opsegu 2,071(2) – 2,174(2) Å, odnosno 76,21(8) – 97,10(7) °.

Kristalografski podaci: $[\text{Co}_2(\text{pyr})(\text{bipy})_2(\text{H}_2\text{O})_6]\cdot 2\text{H}_2\text{O}$, $\text{C}_{30}\text{H}_{34}\text{Co}_2\text{N}_4\text{O}_{16}$, $M_r = 824,48$, monoklinični sistem, prostorna grupa $P2_1/n$, $a = 12,516(3)$, $b = 7,589(2)$, $c = 17,907(5)$ Å, $\beta = 100,02(2)$ °, $V = 1674,9(8)$ Å³, $Z = 2$, $F(000) = 848$, $\rho_x = 1,635$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 1,073$ mm⁻¹, 3205 izmerenih refleksija, $R_1 = 3,08$ % za 2807 refleksija sa $I > 2\sigma(I)$, $R_{w2} = 7,98$ % za sve refleksije i 235 utajenih parametara.



Slika. Prikaz strukture duž pravca [010].

Figure. Projection of the structure along [010].

**STRUCTURE OF 1,3-PROPYLENEDIAMMONIUM
poly-[(μ_4 -PYROMELLITATO)CUPRATE(II)] DIHYDRATE,
[H₃N(CH₂)₃NH₃][Cu{C₆H₂(COO)₄}]·2H₂O**

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X-ray crystal structure analysis of the title complex showed that the structure is built up from bridging pyromellitate tetraanions and copper(II) atoms forming a three-dimensional framework with two channel-like voids of different size. The first kind of channels extending parallel to [001] is filled by water molecules (Fig. 2). The second kind of channels is parallel to [110] and [1-10] and accommodates 1,3-propylenediammonium cations (Fig. 1). Cu(II) atoms are in a tetrahedrally distorted square-planar environment consisting of four carboxylate O atoms from four different pyromellitate ligands. The uncoordinated O atoms from the same carboxylate groups are placed around Cu(II) at longer distances (≈ 2.8 Å) forming a distorted sphenoid.

Crystal data are as follows: C₁₃H₁₈CuN₂O₁₀, $M_r = 425.83$, orthorhombic system, space group $Cc2m$, $a = 8.887(1)$, $b = 11.493(2)$, $c = 16.457(3)$ Å, $V = 1680.9(5)$ Å³, $Z = 4$, $F(000) = 876$, $\rho_x = 1.683$ g cm⁻³, $\mu = 1.358$ mm⁻¹, $R_1 = 0.0303$ for 1012 reflections with $I > 2\sigma(I)$, $wR_2 = 0.0493$ for 1317 independent reflections and 123 refined parameters. The structure was solved by direct methods. During the refinement Flack parameter was about 0.4 for one set of coordinates and about 0.6 for inverted structure. Therefore, after all non-hydrogen atoms have been located and refined anisotropically the refinement of racemic twinning was attempted. The inclusion of twin improved the refinement giving the final twin ratio of 1:1.5.

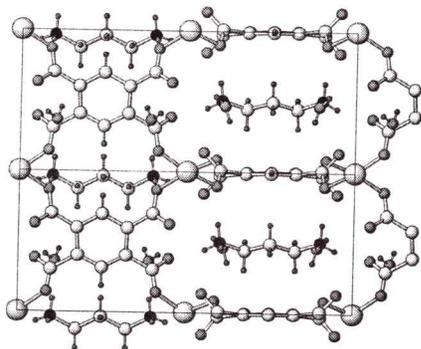


Fig. 1. Projection of the structure along [110].

Sl. 1. Prikaz strukture duž pravca [110].

**STRUKTURA 1,3-PROPILENDIAMONIUM
poly-[(μ_4 -PIROMELITATO)KUPRATA(II)]-DIHIDRATA,
[H₃N(CH₂)₃NH₃][Cu{C₆H₂(COO)₄}]·2H₂O**

D. Poleti ^a, Lj. Karanović ^b

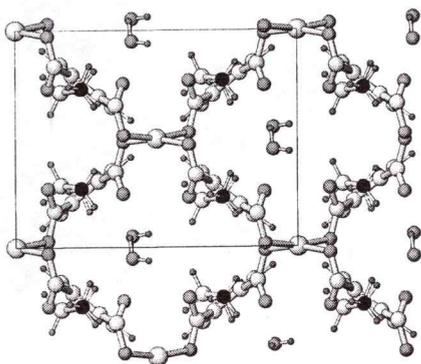
^a Tehnološko-metalurški fakultet, Karnegijeva 4, Beograd, Srbija i Crna Gora,

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Rendgenska strukturna analiza kompleksnog jedinjenja [H₃N(CH₂)₃NH₃][Cu{C₆H₂(COO)₄}]·2H₂O pokazala je da je struktura izgrađena od mostovnih piromelitat-jona i atoma bakra(II), koji formiraju trodimenzionalni skelet sa dve vrste kanala različite veličine. Jedna vrsta kanala paralelna je sa pravcem [001] i sadrži molekule vode (Sl. 2). Druga vrsta kanala pruža se duž pravaca [110] i [1-10] i sadrži 1,3-propilendiamonijum katjone (Sl. 1). Atomi Cu(II) nalaze se u tetraedarski deformisanom kvadratno-planarnom okruženju koji čine četiri karboksilatna O atoma iz četiri različita piromelitat-jona. Nekoordinirani O atomi iz ista četiri piromelitat-liganda smešteni su oko Cu(II) na dužem rastojanju ($\approx 2,8$ Å) i formiraju deformisani sfenoid.

Kristalografski podaci: C₁₃H₁₈CuN₂O₁₀, $M_r = 425,83$, rombični sistem, prostorna grupa *Cc*2*m*, $a = 8,887(1)$, $b = 11,493(2)$, $c = 16,457(3)$ Å, $V = 1680,9(5)$ Å³, $Z = 4$, $F(000) = 876$, $\rho_x = 1,683$ g cm⁻³, $\mu = 1,358$ mm⁻¹, $R_1 = 0,0303$ za 1012 refleksija sa $I > 2\sigma(I)$, $wR_2 = 0,0493$ za 1317 nezavisnih refleksija i 123 utičnjavana parametara. Struktura je rešena direktnim metodama. Tokom utičnjavanja Flakov parametar iznosio je oko 0,4 za jedan set koordinata i oko 0,6 za „invertovanu“ strukturu. Zbog toga je struktura utičnjavana kao racematski blizanac. Uvođenjem bližnjenja rezultati su poboljšani i konačno je nađeno da je odnos dve blizne individue 1:1,5.



Sl. 2. Prikaz strukture duž pravca [001].
Fig. 2. Projection of the structure along [001].

SYNTHESIS AND CRYSTAL STRUCTURE OF [Pd(pap)(py)](ClO₄)₂

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It is well known that the complex compounds of palladium(II) are usually used as a model for better understanding the interactions of platinum(II) complexes, taking into account that the first are 10³ – 10⁵ times more reactive than the second ones.¹

Here we report the synthesis and crystal structure of [Pd(pap)(py)](ClO₄)₂ complex, where pap = bis(2-pyridilmethyl)amine. The metal coordination sphere is square-planar with the expected deviation from right angles around palladium. Also, the distance between the Pd and N(2) is shorter than the distances between the Pd and N(1) and N(3) atoms, what is a typical property for tridentate-coordinated NNN donor ligands to Pd(II) or Pt(II).² Crystal system is triclinic with space group P $\bar{1}$. The structure of complex is shown in Fig. 1.

The two perchlorate ions are located upper and below the plane of complex and the nearest oxygen is about 2.125 Å far from the hydrogen atom H100. In the crystal there are few hydrogen bonds shown in Fig. 2.

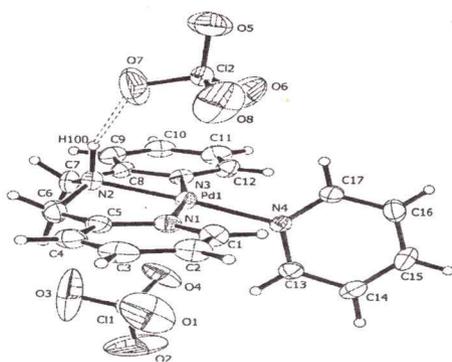


Figure 1.

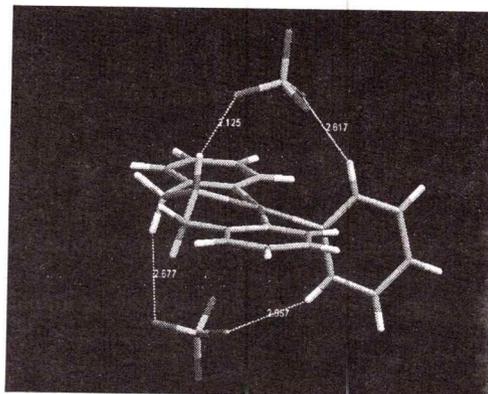


Figure 2.

1. T. Rau, R. van Eldik, in A. Sigel and H. Sigel (Eds), *Metal Ions in Biological Systems*, Marcel Dekker, New York, 1996, 32, 339.
2. Ž. D. Bugarčić, B. Petrović, E. Zangrando, *Inorg. Chim. Acta*, 2004, 357, 9, 2650.

**CRYSTAL STRUCTURE OF
(ETHYLENEDIAMMONIUM-*N,N'*-DI-3-PROPANOIC ACID)
TETRACHLOROPLATINATE (II) COMPLEX**

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The title compound was obtained in reaction of potassium tetrachloroplatinate(II) and ethylenediamine-*N,N'*-di-3-propanoic acid in molar ratio 1 : 1, at room temperature. This is the first example of the platinum(II) complex with this potentially tetradentate ligand.

Crystallographic data: PtC₈H₁₈Cl₄N₂O₄, monoclinic system, space group P2₁/n, a = 8.181(3) Å, b = 10.303(5) Å, c = 9.073(6) Å, α = γ = 90°, β = 103.20(10)°, V = 744.5(7) Å³, z = 2, D_c = 2,423 Mg/m³, μ(MoKα) = 1.547 mm⁻¹, F(000) = 516, no. of parameters: 89, R = 0.0797 and wR2 = 0.2378 (for 1332 reflections with I > 2σI).

The complex (I) consists of two species: [PtCl₄]²⁺ and H₄eddp²⁺ ions (Fig. 1). The platinum atom is found in square-planar geometry with four chloride atoms. The Cl-Pt-Cl angle deviate from the ideal values of 90° with respect to *cis*-coordinated Cl atoms which can be explained with intramolecular and intermolecular hydrogen bond interactions between N1-H1...Cl1 (H...A = 2.730 Å), N1-H2...Cl2 (H...A = 2.767 Å), O1-H1...Cl1 (H...A = 2.734 Å) and O1-H1...Cl2 (H...A = 2.846 Å). The whole H₄eddp²⁺ ion is nearly linear. In the axial positions of platinum atom are found -CH₂-CH₂-COOH parts of H₄eddp²⁺ ion in the direction of equatorial plane.

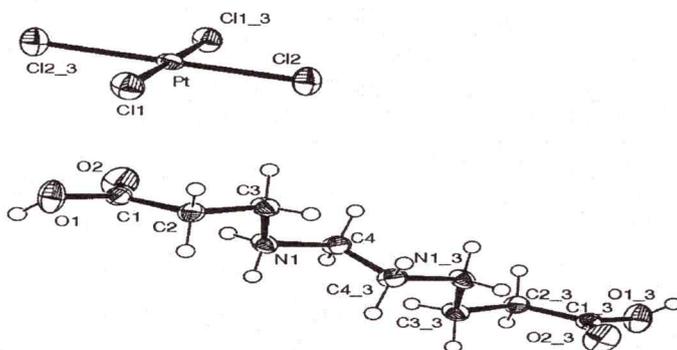


Fig. 1. Structure of H₄eddp[PtCl₄] complex

KRISTALNA STRUKTURA (ETILENDIAMONIUM-*N,N'*-DI-3- PROPIONSKA KISELINA)-TETRAHLOROPLATINAT(II) KOMPLEKSA

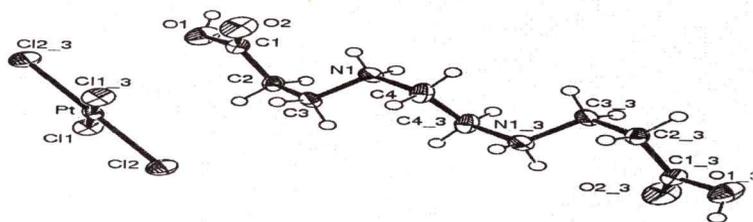
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Kompleks $H_4eddp[PtCl_4]$ je dobijen u reakciji kalijum-tetrahlороplatinata(II) i etilendiamin-*N,N'*-di-3-propionske kiseline u molskom odnosu 1 : 1, na sobnoj temperaturi. Ovo je prvi kompleks platine(II) sa ovim tetradentatnim nekoordinovanim ligandom.

Kristalografski podaci: $PtC_8H_{18}Cl_4N_2O_4$, monoklinički, prostorna grupa $P2_1/n$, $a = 8,181(3) \text{ \AA}$, $b = 10,303(5) \text{ \AA}$, $c = 9,073(6) \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 103,20(10)^\circ$, $V = 744,5(7) \text{ \AA}^3$, $z = 2$, $D_c = 2,423 \text{ Mg/m}^3$, $\mu(MoK\alpha) = 1,547 \text{ mm}^{-1}$, $F(000) = 516$. Opseg: $12,141 < \theta < 15,814^\circ$, broj parametara: 89, $R = 0,0797$, $wR2 = 0,2378$ za 1332 refleksija sa $I > 2\sigma I$.

Kompleks se sastoji od dve vrste: $[PtCl_4]^{2+}$ i H_4eddp^{2+} jona (Slika 1). Atom platine se nalazi u kvadratno-planarnom okruženju sa četiri hlorova atoma. Cl-Pt-Cl uglovi odstupaju od ortogonalnog ugla od 90° (to se može objasniti inter i intramolekulskim interakcijama: $N1 \cdots Cl1$ ($H \cdots A = 2.730 \text{ \AA}$), $N1-H2 \cdots Cl2$ ($H \cdots A = 2.767 \text{ \AA}$), $O1-H1 \cdots Cl1$ ($H \cdots A = 2.734 \text{ \AA}$) i $O1-H1 \cdots Cl2$ ($H \cdots A = 2.846 \text{ \AA}$)). H_4eddp^{2+} jon je približno planaran. Na aksijalnim položajima atom platine ima po dva -CH₂-CH₂-COOH fragmenta, H_4eddp^{2+} jona, paralelno postavljena prema ekvatorijalnoj koordinacionoj ravni.



Slika 1. Struktura $H_4eddp[PtCl_4]$ kompleksa

CRYSTAL STRUCTURE OF GARNET FROM AMPHIBOLITE OF KOKRE LOCALITY

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A general structure formula for garnets is $X_3Y_2Z_3O_{12}$ where X, Y and Z are occupied by different cations. X cations are in irregular hexahedral, Y cations are in octahedral, while Z cations are in tetrahedral coordination of oxygen ions. Two X, one Y and one Z cations that form almost regular tetrahedra surround oxygen anions. Those tetrahedra Z, occupied mainly by Si^{4+} in natural garnets, does not share corners, and therefore garnets are classified as nesosilicates.

According to the already mentioned structure formula investigated garnet is defined with $X = Fe^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+}$, $Y = Al^{3+}$ and $Z = Si^{4+}$. Refined values of site occupation parameters indicate that mass ratios of different garnet components in the investigated crystal are: 53.42 % almandine, 29.64 % grossular, 8.14 % pyrope and 8.79 % spessartine. Agreement between refined values of site occupation factors and chemical analysis results is good. Calculated interatomic distances ($X-O = 2.249(4)$, $Al-O = 1.905(3)$ and $Si-O = 1.641(3)$ Å) are in good agreement to the sum of ionic radii from the obtained cation distribution ($X-O = 2.225$, $Al-O = 1.915$ and $Si-O = 1.64$ Å).

Crystal data: $(Fe_{1.64}^{2+}Ca_{0.91}^{2+}Mg_{0.25}^{2+}Mn_{0.27}^{2+})_{3.07}Al_2^{3+}Si_3^{4+}O_{12}$, Mr = 79.3, cubic crystal system, space group $Ia\bar{3}d$, $Z = 48$, $F(000) = 1863.6$, $\rho_x = 4.01$ g cm⁻³, $\mu(MoK\alpha) = 4.764$ mm⁻¹, $\lambda = 0.71069$ Å, SIEMENS-BRUKER P3-P4 diffractometer, crystal dimension: 0.15 x 0.15 x 0.15 mm, unit cell parameters: $a = 11.633(1)$ Å, $V = 1574.26(3)$ Å³, 192 measured and independent reflections measured by $\omega/2\theta$ scan with average $I/\sigma(I) = 36.76$, $R_\sigma = 0.0272$, $R_1 = 0.050$ for 141 reflections with $I > 2\sigma(I)$, $R_{w2} = 0.077$ (refined on F^2) for all reflections and 18 refined parameters with $\Delta\rho_{max} = 0.660$, $\Delta\rho_{min} = -0.656$ eÅ⁻³, $GOOF = 1.164$. Absorption (empirical Ψ scan; $0 < \Psi < 360^\circ$, $\Delta\Psi = 10^\circ$ on the basis of three reflections) and extinction (extinction parameter $k = 0.0002(2)$) corrections were applied on diffraction data.

KRISTALNA STRUKTURA GRANATA IZ AMFIBOLITA LOKALNOSTI KOKRE

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Strukturna formula granata može se predstaviti opštim izrazom $X_3Y_2Z_3O_{12}$ gde su X, Y i Z položaji koje zauzimaju različiti katjoni. X katjoni su u nepravilnoj heksaedarskoj, Y katjoni se nalaze u oktaedarskoj, dok su Z u tetraedarskoj koordinaciji kiseonika. Kiseonik se nalazi u okruženju dva X, jednog Y i jednog Z katjona, koji čine gotovo pravilan tetraedar. Pošto ti tetraedri, u kojima kod prirodnih granata dominira Si^{4+} , nemaju zajedničke rogljeve, granati su klasifikovani kao nezosilikati.

Prema navedenoj strukturalnoj formuli ispitivani granat se može definisati sa $X = Fe^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+}$, $Y = Al^{3+}$ i $Z = Si^{4+}$. Utačnjene vrednosti faktora zauzeća pokazuju sledeće procentne udele granatskih komponenata: 53,42 % almandina, 29,64 % grosulara, 8,14 % piropa i 8,79 % spesartina. Slaganje utaćnjenih vrednosti faktora zauzeća sa rezultatima hemijske analize je dobro. Izračunata međuatomska rastojanja ($X-O = 2,249(4)$, $Al-O = 1,905(3)$ i $Si-O = 1,641(3)$ Å) dobro se slažu sa sumom jonskih radijusa dobijene katjonske raspodele ($X-O = 2,225$, $Al-O = 1,915$ i $Si-O = 1,64$ Å).

Kristalografski podaci: $(Fe_{1,64}^{2+}Ca_{0,91}^{2+}Mg_{0,25}^{2+}Mn_{0,27}^{2+})_{3,07}Al_2^{3+}Si_3^{4+}O_{12}$, $Mr = 79,3$,

teseralni kristalni sistem, prostorna grupa $Ia\bar{3}d$, $Z = 48$, $F(000) = 1863,6$, $\rho_x = 4,01$ g cm⁻³, $\mu(MoK\alpha) = 4,764$ mm⁻¹, $\lambda = 0,71069$ Å, SIEMENS-BRUKER P3-P4 difraktometar, dimenzije kristala: 0,15 x 0,15 x 0,15 mm, parametri jedinične ćelije: $a = 11,633(1)$ Å, $V = 1574,26(3)$ Å³, 192 izmerene i nezavisne refleksije merene $\omega/2\theta$ skanom sa srednjim $I/\sigma(I) = 36,76$, $R_\sigma = 0,0272$, $R_1 = 0,050$ za 141 refleksiju sa $I > 2\sigma(I)$, $R_{w2} = 0,077$ (utačnjavanje pomoću F^2) za sve refleksije i 18 utaćnjenih parametara sa $\Delta\rho_{max} = 0,660$, $\Delta\rho_{min} = -0,656$ eÅ⁻³, $GOOF = 1,164$. Podaci su korigovani za apsorpciju empirijskom metodom (Ψ skan; $0 < \Psi < 360^\circ$, $\Delta\Psi = 10^\circ$) na osnovu tri refleksije, i za ekstinkciju (parametar za ekstinkciju $k = 0,0002(2)$).

A METHOD FOR OBTAINING CRYSTALS IN A CHAMBER FURNACE

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Analysis of a series of methods for obtaining crystals from melts [1], has shown that Stöber's method can be applied in a laboratory chamber furnace. The original apparatus that we have constructed, based on Stöber's method, is shown in figure 1. It enables simultaneous testing of different shapes of crystallization fronts, temperature gradients and intervals of crystallization rates for obtaining crystals.

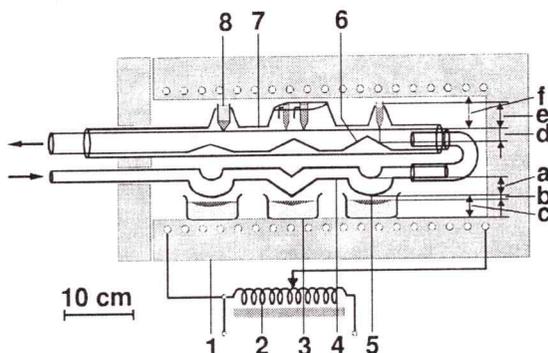


Figure 1. Crystallization apparatus: (1) laboratory chamber furnace, (2) continuously changeable transformer, (3) column of crucibles with the floating crystals, (4) air cooler ("cold shelf"), (5) cold "teeth", (6) cold "thresholds", (7) movable cylindrical tube with mounting holes and groove ("telescopic test sieve") and (8) family group of Tamman's test tubes ("test comb").

The shapes of crystallization fronts and crystallization rates in crucibles are regulated by the path and cross-section of the air flow (a), respectively. The crystallization rates can also be regulated by the distance (b). The crystallization rates in Tamman's test tubes [1] can be regulated by the cross-section of the air flow (d), i.e. the position of the test tubes. The temperature gradients are regulated by the distances (c) and (f). This method can also be applied in a tube furnace in a horizontal position [2].

[1] K.-Th.Wilke, J. Bohm, *Kristallzüchtung*, Deutscher Verlag der Wissenschaften, Berlin, (1988), 591-608.

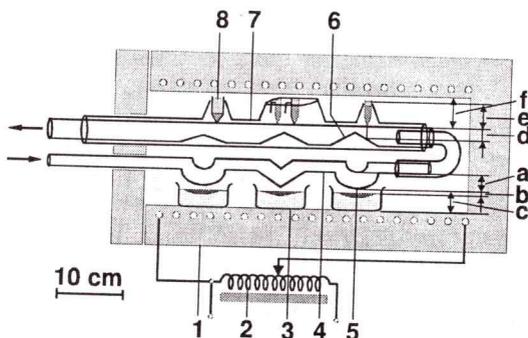
[2] B. Čabrić, T. Pavlović, *J. Appl. Cryst.*, **33** (2000), 387-388.

МЕТОДА ЗА ДОБИЈАЊЕ КРИСТАЛА У КОМОРНОЈ ПЕЋИ

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Од низа метода за добијање кристала из растопа, нашли смо да се у лабораторијској коморној пећи може применити Штеберова (F. Stöber) метода [1]. Оригинална апаратура коју смо конструисали, на основу Штеберове методе, шематски је приказана на слици 1. Она омогућава, симултану пробу неколико различитих облика кристалizacionих фронтва, температурских градијената, и интервала брзина кристализација, за добијање кристала.



Слика 1. Апаратура за кристализацију: (1) лабораторијска коморна пећ, (2) континуално променљив трансформатор, (3) колона тиглова са пливајућим кристалима (4) ваздушни хладњак («хладна полица»), (5) хладни «зуби», (6) хладни «прагови» (7) цилиндрична цев са рупицама и прорезима («телескопско пробно сито») и (8) колона Таманових епрувета («пробни чешаљ»).

Облици кристалizacionих фронтва и брзине кристализације у тигловима се регулишу помоћу путање и попречног пресека ваздушне струје (а), респективно. Брзине кристализације могу се такође регулисати помоћу растојања (b). Брзине кристализација у Тамановим (G. Tamman) епруветама [1] се рефулишу помоћу пресека ваздушне струје (d), тј. положаја епрувета. Температурски градијенти се регулишу помоћу растојања (c) и (f). Ова метода може се применити и у цилиндричној пећи у хоризонталном положају [2].

[1] K.-Th. Wilke, J. Bohm, *Kristallzüchtung*, Deutscher Verlag der Wissenschaften, Berlin (1988), 591-608

[2] Б. Чабрић, Т. Павловић, *Jappl. Cryst.*, **33** (2000), 387-388

NEUTRON POWDER DIFFRACTION ANALYSIS OF $H_3PW_{12}O_{40} \cdot 6D_2O$ IN TEMPERATURE RANGE 259 \leftrightarrow 1.5 K

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Analysed 12-tungstophosphoric hexahydrate acid $H_3PW_{12}O_{40} \cdot 6D_2O$ consists of Keggin's anions $H_3PW_{12}O_{40}^{3-}$ and dioxonium cations $H_5O_2^+$ with two statistically distributed substructures [1]. This acid, stable in specific temperature and water partial pressure ranges, has been studied before at different temperatures between 10 and 350 K [2, 3]. In previous studies it was confirmed that various forms of proton species and hydrated proton entities [4], like products of dissociation/association process according to the dynamic equilibrium equation $H_5O_2^+ \leftrightarrow \leftrightarrow H_3O^+ + H_2O \leftrightarrow H_4^+ + 2H_2O$, could take a part in the structure. Existence of different proton species is essential for biochemical and catalytic properties of these compounds. Conditions that cause change of the balance in the thermal stability of WPA-6 are not known yet. Changes in lattice and molecular structure of this acid induced by temperature treatment were studied *in situ* by neutron powder diffraction (diffractometer G4.1, Orphée nuclear reactor, Laboratoire LLB, Saclay, France).

During the structure refinement, new phase of $H_3PW_{12}O_{40} \cdot 6D_2O$ acid has been detected. This new phase consists of Keggin's anion, but instead of dioxonium cation products of its dissociation - proton and two water molecules exist in the structure. In this research some interesting correlations between changes of atom coordinates, interatomic distances and occupation factors with temperature change have been noticed.

[1] G. Brown, M. Noe-Spirlet, W. Busing, H. Levy, Acta Crystallogr. B33 (1997), pp. 1038-1046

[2] A. Kremenović, A. Spasojević-de Biré, F. Boureé, Ph. Colomban, R. Dimitrijević, M. Davidović, U. B. Mioč, Solid State Ionics, 150 (2002), str. 431-442

[3] A. Kremenović, A. Spasojević-de Biré, R. Dimitrijević, P. Sciau, U. B. Mioč, Ph. Colomban, Solid State Ionics, 132 (2000), str. 39-53

[4] U. B. Mioč, M. Davidović, N. Tjapkin, Ph. Colomban, A. Novak, Solid State Ionics, 46 (1991), str. 103-109

NEUTRONSKA DIFRAKCIJNA ANALIZA POLIKRISTALNOG $H_3PW_{12}O_{40} \cdot 6D_2O$ U TEMPERATURNOM OPSEGU 259 \leftrightarrow 1,5 K

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Ispitivani heksahidrat 12-volframfosforne kiseline $H_3PW_{12}O_{40} \cdot 6D_2O$ sastoji se Keggin-

-ovog anjona $H_3PW_{12}O_{40}^{3-}$ i dioksonijum katjona $H_5O_2^+$ sa dve statistički rasporedjene podstrukture [1]. Ova kiselina, koja je stabilna u određenom opsegu temperature i parcijalnog pritiska vode, ispitivana je na različitim temperaturama između 10 i 350 K [2, 3]. U ranijim istraživanjima je potvrđeno da različite protonske vrste i hidratizirani protonski entiteti [4], kao što su produkti procesa disocijacije/asocijacije prema jednačini dinamičke ravnoteže $H_5O_2^+ \leftrightarrow H_3O^+ + H_2O \leftrightarrow H^+ + 2H_2O$, mogu biti sastavni deo ove strukture. Postojanje različitih protonskih vrsta je osnova svih katalitičkih i biohemijских osobina ovog jedinjenja. Uzroci promene ravnoteže u uslovima termičke stabilnosti heksahidrata WPA još nisu poznati. Promene u rešetci i molekularnoj strukturi ove kiseline indukovane promenom temperature ispitivane su *in situ* neutronsom difrakcijom na prahu (difraktometar G4.1, Orpheé nuklearni reaktor, laboratorija LLB, Saclay, Francuska).

Tokom utučnjavanja strukture otkrivena je nova faza kiseline $H_3PW_{12}O_{40} \cdot 6D_2O$. Nova faza sastoji se od Keggin-ovog anjona, ali umesto dioksonijum katjona sadrži produkte njegove disocijacije - proton i dva molekula vode. U ovom istraživanju primećene su neke interesantne korelacije između promena koordinata atoma, međjuatomskih rastojanja i faktora zauzeća položaja nekih atome sa promenom temperature.

[1] G. Brown, M. Noe-Spirlet, W. Busing, H. Levy, Acta Crystallogr. B33 (1997), str. 1038-1046

[2] A. Kremenović, A. Spasojević-de Biré, F. Boureé, Ph. Colombar, R. Dimitrijević, M. Davidović, U. B. Mioč, Solid State Ionics, 150 (2002), str. 431-442

[3] A. Kremenović, A. Spasojević-de Biré, R. Dimitrijević, P. Sciau, U. B. Mioč, Ph. Colombar, Solid State Ionics, 132 (2000), str. 39-53

[4] U. B. Mioč, M. Davidović, N. Tjapkin, Ph. Colombar, A. Novak, Solid State Ionics, 46 (1991), str. 103-109

CRYSTALLOGRAPHICAL DATA FOR DOLOMITE FROM THE WHITE MARBLE KRECANA-VENCAC ORE DEPOSIT

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Using X-ray powder diffraction method it was established that the sample under investigation contains Mg-calcite ($\approx 95\%$), dolomite ($\approx 4\%$) and quartz ($\approx 1\%$).

The values for hkl, I and d for this dolomite are presented in Table 1 and calculated unit cell dimensions in Table 2.

Obtained results were compared with the literature data [1].

Table 1: Values for the hkl, I and d of dolomite.

Keller and McCarthy (1985)			Krecana		
h k l	I_{obs}	d_{obs}	I_{obs}	d_{obs}	d_{calc}
1 0 1	1	4.0330	0.75	4.0154	4.0157
0 1 2	4	3.6990	0.82	3.6673	3.6809
1 0 4	100	2.8880	4.11	2.8702	2.8751
0 0 6	4	2.6700	0.83	2.6628	2.6584
0 1 5	3	2.5390	0.78	2.5350	2.5290
1 1 0	7	2.4040	1.13	2.3979	2.3956
1 1 3	19	2.1930	1.13	2.1812	2.1841
0 2 1	3	2.0650	0.62	2.0598	2.0573
2 0 2	10	2.0150	0.98	2.0087	2.0078
0 2 4	3	1.8473	0.78	1.8382	1.8405
0 1 8	10	1.8049	1.13	1.7968	1.7971
1 1 6	13	1.7870	1.13	1.7776	1.7796
2 1 1	2	1.5667	0.51	1.5583	1.5608
1 2 2	4	1.5446	7.52	1.5425	1.5388

Table 2: Calculated unit cell dimensions of dolomite.

	Keller and McCarthy (1985)	Krecana
a_0 (Å)	4.809	4.791(3)
c_0 (Å)	16.02	15.95(2)
V_0 (Å ³)	320.88	317.1(4)

From Tables 1 and 2 it can be seen that the d-values and unit cell dimensions of the dolomite from Krecana are considerable smaller than the literature data [1]. Using different calculations, from the mineralogical and chemical compositions it was established that dolomite is Ca-deficit, i.e. that exchangings of $CaCO_3$ with $MgCO_3$ and $FeCO_3$ are about 3-5 mol.% [2].

[1] Keller, L. and McCarthy, G., (1985): JCPDS 36-0426, Dolomite, North Dakota State Univ., Fargo, ND, USA, ICDD Grant-In-Aid.

[2] Tancic, P., Cvetkovic, Z. and Markovic, I.: Mg-calcite and dolomite from the white marble Krecana-Vencac ore deposit, Part II: Chemical composition and origin temperature, (in press).

KRISTALOGRAFSKI PODACI ZA DOLOMIT IZ BELOG MERMERA LEŽIŠTA KREČANA-VENČAC

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Rendgenskom difrakcionom metodom praha utvrđeno je da se ispitivani uzorak sastoji od Mg-kalcita ($\approx 95\%$), dolomita ($\approx 4\%$) i kvarca ($\approx 1\%$).

Vrednosti za hkl, I i d ovog dolomita prikazane su u Tabeli 1, a izračunate dimenzije jedinične ćelije u Tabeli 2.

Dobijeni rezultati su upoređeni sa podacima iz literature [1].

Tabela 1: Vrednosti za hkl, I i d dolomita

Keller i McCarthy (1985)			Krečana		
h k l	I_{izm}	d_{izm}	I_{izm}	d_{izm}	d_{izr}
1 0 1	1	4,0330	0,75	4,0154	4,0157
0 1 2	4	3,6990	0,82	3,6673	3,6809
1 0 4	100	2,8880	4,11	2,8702	2,8751
0 0 6	4	2,6700	0,83	2,6628	2,6584
0 1 5	3	2,5390	0,78	2,5350	2,5290
1 1 0	7	2,4040	1,13	2,3979	2,3956
1 1 3	19	2,1930	1,13	2,1812	2,1841
0 2 1	3	2,0650	0,62	2,0598	2,0573
2 0 2	10	2,0150	0,98	2,0087	2,0078
0 2 4	3	1,8473	0,78	1,8382	1,8405
0 1 8	10	1,8049	1,13	1,7968	1,7971
1 1 6	13	1,7870	1,13	1,7776	1,7796
2 1 1	2	1,5667	0,51	1,5583	1,5608
1 2 2	4	1,5446	7,52	1,5425	1,5388

Tabela 2: Izračunate dimenzije jedinične ćelije dolomita

	Keller i McCarthy (1985)	Krečana
a_0 (Å)	4,809	4,791(3)
c_0 (Å)	16,02	15,95(2)
V_0 (Å ³)	320,88	317,1(4)

Iz Tabela 1 i 2 može se videti da su d-vrednosti i dimenzije jedinične ćelije dolomita iz Krečane značajno manje od literaturnih podataka [1]. Na osnovu mineraloškog i hemijskog sastava utvrđeno je različitim proračunima da je dolomit Ca-deficitaran, t.j. da zamenjivanje CaCO_3 sa MgCO_3 i FeCO_3 iznosi oko 3-5 mol.% [2].

[1] Keller, L. and McCarthy, G., (1985): JCPDS 36-0426, Dolomite, North Dakota State Univ., Fargo, ND, USA, ICDD Grant-In-Aid.

[2] Tančić, P., Cvetković, Ž. i Marković, I.: Mg-kalcit i dolomit iz belog mermera ležišta Krečana-Venčac, Deo II: Hemijski sastav i temperature postanka, (u štampi).

RESULTS OF THE PRELIMINARY INVESTIGATIONS OF GARNET FROM STARA PLANINA Mt.

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Garnet from the garnet - amphibole association at Stara Planina Mt. was investigated by the X-ray powder diffraction method.

The values for hkl, I and d are presented in Table 1, and calculated unit cell dimensions at Table 2.

Obtained results were compared with the literature data [1].

Table 1: Values for the hkl, I and d of garnet

Yoder and Keith (1951)		Stara planina		Yoder and Keith (1951)		Stara planina	
h k l	d _{izm}	d _{izm}	d _{izr}	h k l	d _{izm}	d _{izm}	d _{izr}
2 1 1	4.760	4.780	4.762	6 2 0	1.836	1.843	1.844
3 2 1	3.100	3.120	3.117	5 4 1	1.797	1.800	1.800
4 0 0	2.910	2.919	2.916	6 3 1	1.710	1.719	1.720
4 2 0	2.600	2.611	2.608	4 4 4	1.681	1.684	1.684
3 3 2	2.480	2.488	2.487	5 4 3	1.650	1.650	1.650
4 2 2	2.370	2.383	2.381	6 4 0	1.614	1.617	1.618
4 3 1	2.280	2.288	2.288	7 2 1	1.586	1.587	1.587
5 2 1	2.130	2.129	2.130	6 4 2	1.557	1.558	1.559
4 4 0	2.060	2.061	2.062	6 5 1	1.482	/	/
6 1 1	1.886	1.892	1.892	8 0 0	1.456	1.458	1.458

Table 2: Calculated unit cell dimensions of garnet

	Yoder and Keith (1951)	Stara planina
a ₀ (Å)	11.63	11.664(1)
V ₀ (Å ³)	1573.04	1586.9(6)

From Tables 1 and 2 it can be seen that the values of the interplanar spacings (d) and unit cell parameters (a₀ and V₀) of the investigated garnet from Stara Planina Mt. are approximative to the values of the garnet of the spessartine type [1], however they are slightly bigger.

These slightly bigger values probably indicate the possible partial transition toward the garnet of the grossular type, e.g. the exchanging of Mn²⁺ with Ca²⁺.

The other investigations are in progress and the results will be published afterwards.

[1] Yoder, H. and Keith, (1951): JCPDS 10-0354, Spessartine, Am. Mineral., 36, 529.

REZULTATI PRELIMINARNIH ISPITIVANJA GRANATA SA STARE PLANINE

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Granat iz granatsko - amfibolske asocijacije na Staroj planini ispitivan je rendgenskom difrakcionom metodom praha.

Vrednosti za hkl, I i d prikazane su u Tabeli 1, a izračunate dimenzije jedinične ćelije u Tabeli 2.

Dobijeni rezultati su upoređeni sa podacima iz literature [1].

Tabela 1: Vrednosti za hkl, I i d granata

Yoder i Keith (1951)		Stara planina		Yoder i Keith (1951)		Stara planina	
h k l	d_{izm}	d_{izm}	d_{izr}	h k l	d_{izm}	d_{izm}	d_{izr}
2 1 1	4,760	4,780	4,762	6 2 0	1,836	1,843	1,844
3 2 1	3,100	3,120	3,117	5 4 1	1,797	1,800	1,800
4 0 0	2,910	2,919	2,916	6 3 1	1,710	1,719	1,720
4 2 0	2,600	2,611	2,608	4 4 4	1,681	1,684	1,684
3 3 2	2,480	2,488	2,487	5 4 3	1,650	1,650	1,650
4 2 2	2,370	2,383	2,381	6 4 0	1,614	1,617	1,618
4 3 1	2,280	2,288	2,288	7 2 1	1,586	1,587	1,587
5 2 1	2,130	2,129	2,130	6 4 2	1,557	1,558	1,559
4 4 0	2,060	2,061	2,062	6 5 1	1,482	/	/
6 1 1	1,886	1,892	1,892	8 0 0	1,456	1,458	1,458

Tabela 2: Izračunate dimenzije jedinične ćelije granata

	Yoder i Keith (1951)	Stara planina
a_0 (Å)	11,63	11,664(1)
V_0 (Å ³)	1573,04	1586,9(6)

Iz Tabela 1 i 2 može se videti da su vrednosti međujupljiosnih rastojanja (d) i parametri jedinične ćelije (a_0 i V_0) ispitivanog granata sa Stare planine približne vrednostima granata spesartinskog tipa [1], s tim što su nešto veće.

Ove nešto veće vrednosti najverovatnije ukazuju na delimični prelaz ka granatu grosularskog tipa, odnosno na delimičnu zamenu Mn^{2+} sa Ca^{2+} .

Ostala ispitivanja su u toku i rezultati će biti objavljeni naknadno.

[1] Yoder, H. and Keith, (1951): JCPDS 10-0354, Spessartine, Am. Mineral., 36, 529.

RELATION BETWEEN THE CRYSTALLOGRAPHIC PARAMETERS AND THE FeS AND CuS CONTENTS AT SPHALERITES FROM KIZEVAK

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At sphalerites from Kizevak there were determined crystallographic parameters, and the FeS and CuS contents in order to establish what is their mutually relation.

Obtained results of these investigations are presented Table 1.

Table 1: Crystallographical parameters and the FeS and CuS contents (in mol. %)

	FeS	CuS	a_0 (Å)	V_0 (Å ³)
15.635 yellow	1.29	0.01	5.4184(6)	159.08(5)
15.633 yellow	1.67	0.05	5.4185(5)	159.09(4)
15.623 yellow	2.12	0.03	5.4186(4)	159.10(4)
15.611 brownish-yellow	2.22	0.04	5.4186(6)	159.10(5)
15.634 brown	4.53	0.18	5.4187(5)	159.10(5)
15.629 brown	6.39	0.05	5.4190(5)	159.14(5)
15.604 brown	8.17	0.30	5.4189(4)	159.13(3)
15.611 brownish-red	12.28	0.05	5.4195(6)	159.18(6)

It was confirmed that the unit cell dimensions of sphalerites increase with increase of the FeS content, which is well known from many literature datas ([1], [2], [3], [4], [5], etc.). However, at sphalerites from Kizevak the unit cell dimensions are considerably bigger related to [1], [3] and [5]. That isn't much unusual, because [2] and [4] indicated to the similar disagreement, and also because this problematic was not yet completely resolved.

On the other hand, at the samples 15.634 and 15.604 there is partially decrease of the crystallographical parameters related to the other samples, which was most probably caused by the bigger CuS content (0,18 and 0,30 mol.%), and at which indicate literature datas [6], [7] and [8].

[1] Kullerud, G., (1953): Norsk Geologisk Tidsskrift, 32, 61-147.

[2] Jankovic, S. and Jankovic-Milosavljevic, R., (1955): Zbornik Radova Geoloskog i Rudarskog Fakulteta, 3, 19-23.

[3] Skinner, B. J., Barton, P. B., Jr. and Kullerud, G., (1959): Econ. Geol., 54, 1040-1046.

[4] Krstanovic, I. and Krstanovic, M., (1962): V Savetovanje Geologa SFRJ, II, 7-10.

[5] Barton, P. B., Jr. and Toulmin, P., III, (1966): Econ. Geol., 61, 815-849.

[6] Toulmin, P., III, (1960): Geol. Soc. of Am. Bull., 71, 1993.

[7] Wiggins, L. B. and Craig, J. R. (1980): Econ. Geol., 75, 742-751.

[8] Toulmin, P., III, Barton, P. B., Jr., and Wiggins, L. B. (1991): Am. Min., 76, 1038-1051.

ODNOS IZMEDJU KRISTALOGRAFSKIH PARAMETARA I SADRŽAJA FeS I CuS KOD SFALERITA IZ KIŽEVAKA

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Kod sfalerita iz Kiževaka određeni su kristalografski parametri i sadržaji FeS i CuS da bi se utvrdilo u kakvom su međusobnom odnosu.

Dobijeni rezultati ovih ispitivanja su prikazani u Tabeli 1.

Tabela 1: Kristalografski parametri i sadržaji FeS i CuS (u mol. %)

	FeS	CuS	a_0 (Å)	V_0 (Å ³)
15.635 `ut	1,29	0,01	5,4184(6)	159,08(5)
15.633 `ut	1,67	0,05	5,4185(5)	159,09(4)
15.623 `ut	2,12	0,03	5,4186(4)	159,10(4)
15.611 mrko-`ut	2,22	0,04	5,4186(6)	159,10(5)
15.634 mrk	4,53	0,18	5,4187(5)	159,10(5)
15.629 mrk	6,39	0,05	5,4190(5)	159,14(5)
15.604 mrk	8,17	0,30	5,4189(4)	159,13(3)
15.611 mrko-crven	12,28	0,05	5,4195(6)	159,18(6)

Potvrđeno je da dimenzije jediničnih ćelija sfalerita rastu sa porastom sadržaja FeS, kao što je dobro poznato iz mnogih literaturnih podataka ([1], [2], [3], [4], [5], itd.). Međutim, kod sfalerita iz Kiževaka dimenzije jediničnih ćelija su značajno veće u odnosu na [1], [3] i [5]. To nije mnogo neuobičajeno, jer su [2] i [4] ukazali na slična neslaganja, a i zbog toga što ova problematika još nije u potpunosti razrešena.

Sa druge strane, kod uzoraka 15.634 i 15.604 postoji delimično smanjenje kristalografskih parametara u odnosu na ostale uzorke, što je najverovatnije prouzrokovano većim sadržajem CuS (0,18 i 0,30 mol.%), a na šta ukazuju literaturni podaci [6], [7] i [8].

- [1] Kullerud, G., (1953): Norsk Geologisk Tidsskrift, 32, 61-147.
[2] Janković, S. i Janković-Milosavljević, R., (1955): Zbornik Radova Geološkog i Rudarskog Fakulteta, 3, 19-23.
[3] Skinner, B. J., Barton, P. B., Jr. and Kullerud, G., (1959): Econ. Geol., 54, 1040-1046.
[4] Krstanović, I. i Krstanović, M., (1962): V Savetovanje Geologa SFRJ, II, 7-10.
[5] Barton, P. B., Jr. and Toulmin, P., III, (1966): Econ. Geol., 61, 815-849.
[6] Toulmin, P., III, (1960): Geol. Soc. of Am. Bull., 71, 1993.
[7] Wiggins, L. B. and Craig, J. R. (1980): Econ. Geol., 75, 742-751.

[8] Toulmin, P., III, Barton, P. B., Jr., and Wiggins, L. B. (1991): *Am. Min.*, 76, 1038-1051.

REFINEMENT OF CRYSTAL STRUCTURE OF ROCHELLE SALT

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Rochelle salt, sel de Seignette (1675) or the sodium potassium tartrate ($\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$), is the substance in which ferroelectricity was discovered for the first time. Because of very wide group of tartarates that are possible to crystallize and their different ferroelectric behaviour, its structure was object of investigation by various authors through years [1, 2]. Besides that Rochelle salt shows domain crystal structure as a consequence of different parameters of crystallization. Domain structure could be induced even during preparation of specimens for XRPD investigations.

Refinement of crystal structure of Rochelle salt above temperature of Curie point was done. Data were collected with Sintex P-1 diffractometer for single crystal, using X-ray Mo $K\alpha$ radiation, up to $55^\circ \theta$. The sodium potassium tartrate crystallize in orthorhombic *S. G.* $P2_22_1$ with unit cell dimensions $a = 6.239(2) \text{ \AA}$, $b = 11.897(3) \text{ \AA}$, $c = 14.276(4) \text{ \AA}$, and $V = 1060(10) \text{ \AA}^3$. Positions of hydrogens were found from the difference map, and partially refined. From literature it is known that position of hydrogens were solved only by neutron diffraction on single crystal [3]. At final stage of refinement values of R_1 (all) and $GofF$ were 0.045 and 1.24, respectively.

- [1] I. Krstanović et al, *Bull. Acad. Serbe Sci. Mat. Nat.*, 32 (1963), p. 149-150
[2] X. Solans et al, *J. Solid State Chemistry*, 131 (1997), p. 350-359
[3] E. Suzuki et al, *Ferroelectrics*, 152 (1994), p. 385-390

УТАЧЊАВАЊЕ КРИСТАЛНЕ СТРУКТУРЕ РОШЕЛСКЕ СОЛИ

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Рошелска со, Сењетова со (1675) или натријум калијум тартарат ($\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$), је хемијско једињење на којем је фероелектрицитет пронађен први пут. Услед великог броја једињења у групи тартарата која кристалишу и њиховог различитог фероелектричног понашања, њихове структуре су биле годинама предмет истраживања разних аутора [1, 2]. Поред тога Рошелска со показује доменску кристалну структуру као последицу различитих параметара кристализације. Доменска структура може се изазвати чак и приликом припремања препарата за рендгенску дифракцију на поликристалном узорку.

Утачњена је структура Рошелске соли изнад температуре Киријеве тачке. Подаци су прикупљени помоћу Sintex P-1 дифрактометра за монокристал, користећи рендгенско Мо Ка зрачење до $55^\circ \theta$. Натријум калијум тартарат кристалише у ромбичној просторној групи $P 2_2 2_1$ са параметрима елементарне ћелије: $a = 6.239(2) \text{ \AA}$, $b = 11.897(3) \text{ \AA}$, $c = 14.276(4) \text{ \AA}$, и $V = 1060(10) \text{ \AA}^3$. Положајеви водоника одређени су из диферентне мале и делимично су утачњавани. Из литературе је познато да су положајеви водоника решени неутронском дифракцијом на монокристалу [3]. На крају утачњавања одговарајуће вредности R_1 (all) и $GofF$ били су 0,045 и 1,24.

[1] I. Krstanović et al, Bull. Acad. Serbe Sci. Mat. Nat, 32 (1963), p. 149-150

[2] X. Solans et al, J. Solid State Chemistry, 131 (1997), p. 350-359

[3] E. Suzuki et al, Ferroelectrics, 152 (1994), p. 385-390

MODULATIONS IN STRUCTURE OF PURE SODIUM NEPHELINES

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Nepheline $(K,Na)SiAlO_4$ is mineral from feldspatoide group. It is stuffed derivative of tridymite structure, where interstitial positions are occupied with Na and K. In nature, up to one quarter of those positions are occupied by potassium. Pure sodium nephelines with different Si/Al ratio were synthesized and investigated in the form of monocrystal in space group $P 6_3$ [1]. Some of natural and synthetic nephelines show domain structure [2].

Applying zeolite thermally induced transformation three samples of sodium nephelines were synthesized. Depending on chemical composition of starting zeolites: Na-LTA (zeolite 4A, Si/Al = 1.00), Na-FAU (zeolite 13X, Si/Al = 1.24) and Na-GIS (zeolite P, Si/Al = 1.50), one stoichiometric and two nonstoichiometric nephelines were obtained [3]. XRPD data for these specimens at low 2θ values were recorded, in order to investigate additional satellite reflections, that are present in them, as a result of modulated structure. Three different specimens of Na-LTA obtained at 900, 1100, and 1200 °C, were mutually compared. On the other hand they were compared with Na-FAU, and Na-GIS nephelines, obtained at 1000 °C. Even though right space group or modulation was not determined, results show consistency in both cases.

[1] B. Hippler, H. Böhm, Z. Kristall, 187 (1989), p. 39-53

[2] J. Parker, Z. Kristall, 136 (1972), p. 255-272

[3] R. Dimitrijević et al, J. Phys. Chem. Sol, 65(10) (2004), p. 1623-1633

МОДУЛАЦИЈЕ У СТРУКТУРИ ЧИСТИХ Na НЕФЕЛИНА

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Нефелин (K,Na)SiAlO₄ је минерал из групе фелдспатоида. Он је попуњени дериватив тридимитског типа структуре, где су интерстицијски положајеви попуњени са Na и K. У природи је до једне четвртине ових положајева заузима K. Чисти Na нефелини са различитим односом Si/Al су синтетизовани и испитивани у облику монокристала у просторној групи *P* 6₃ [1]. Неки од природних и синтетичких нефелина показују доменску структуру [2].

Три различита узорка Na нефелина су синтетисана применом термално индуковане трансформације зеолита. У зависности од хемијског састава полазних зеолита: Na-LTA (зеолит 4A, Si/Al = 1.00), Na-FAU (зеолит 13X, Si/Al = 1.24) и Na-GIS (зеолит P, Si/Al = 1.50), добијени су један стехиометријски и два нестехиометријска нефелина [3]. Да би се испитале додатне сателитске рефлексије извршена је рендгенска дифракција на праху, на малим угловима 2θ, за поменуте узорке. Сателитске рефлексије су присутне као последица модулисаности структуре. Међусобно су упоређена три различита узорка Na-LTA добијена на 900, 1100 и 1200 °C. Са друге стране они су упоређени са Na-FAU и Na-GIS нефелинима који су добијени на 1000 °C. Резултати су конзистентни у оба поређења иако није утврђена права просторна група и модулација.

[1] В. Hippler, Н. Böhm, Z. Kristall, 187 (1989), p. 39-53

[2] J. Parker, Z. Kristall, 136 (1972), p. 255-272

[3] R. Dimitrijević et al, J. Phys. Chem. Sol, 65(10) (2004), p. 1623-1633

CRYSTAL STRUCTURES OF *TRANS,TRANS*-DIBROMOBIS(*N*-METHYLGLYCINATO)PLATINUM(IV) AND AN UNEXPECTED POLYNUCLEAR COMPLEX

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The reaction between K_2PtBr_6 and sarcosine in the presence of lithium hydroxide led to the crystallization of two complexes, *trans,trans*-[Pt(Sar)₂Br₂] (**1**) and unexpected polynuclear {[Pt(Sar-H)₂Br].H₂O}_n (**2**). Both of metal complexes were characterized by X-ray structural analysis.

Single-crystal data were collected on an Enraf-Nonius CAD-4 diffractometer using Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) and $\omega/2\theta$ scans in 3.13 to 25.98° θ range and 2.40 to 25.96° θ range for complex **1** and complex **2**, respectively. A Gaussian-type absorption correction based on the crystal morphology was applied for both crystal structures ($T_{min} = 0.0422$, $T_{max} = 0.3129$ for **1**; $T_{min} = 0.1261$, $T_{max} = 0.2442$ for **2**). The structures were solved by the heavy atom method and difference Fourier methods and refined on F^2 by full-matrix least-square method. Hydrogen atoms were placed geometrically and refined with a riding model, and with U_{iso} constrained to U_{eq} of the carrier atom.

Crystallographic data for **1**: formula $C_6H_{12}Br_2N_2O_4Pt$, monoclinic, space group $P2_1/a$, $a = 10.921(8) \text{ \AA}$, $b = 9.562(3) \text{ \AA}$, $c = 6.890(5) \text{ \AA}$, $\beta = 125.46(5)^\circ$, $V = 585.5(6) \text{ \AA}^3$, $Z = 2$, $D_c = 3.012 \text{ g/cm}^3$, $\mu = 18.803 \text{ mm}^{-1}$, orange crystal with the dimensions of $0.350 \times 0.300 \times 0.066 \text{ mm}$, $R1 = 0.0711$ and $Rw = 0.1983$ ($GooF = 1.108$) for 72 refined parameters and 869 reflections with $I > 2\sigma(I)$.

Crystallographic data for **2**: formula $C_6H_{12}BrN_2O_4Pt$, monoclinic, space group $C2/m$, $a = 12.362(5) \text{ \AA}$, $b = 5.657(2) \text{ \AA}$, $c = 9.616(4) \text{ \AA}$, $\beta = 118.00(3)^\circ$, $V = 593.8(4) \text{ \AA}^3$, $Z = 2$, $D_c = 2.613 \text{ g/cm}^3$, $\mu = 15.184 \text{ mm}^{-1}$, green crystal with the dimensions of $0.560 \times 0.014 \times 0.011 \text{ mm}$, $R1 = 0.0426$ and $Rw = 0.1078$ ($GooF = 1.170$) for 51 refined parameters and 643 reflections with $I > 2\sigma(I)$.

The complex **1** consists of two identical centrosymmetrically related halves. Octahedral coordination geometry is significantly deformed since that the N-Pt-Br coordination angles [$84.1(4)$ and $95.9(4)^\circ$] deviate extremely from an expected value of 90° .

The complex **2**, {[Pt(Sar-H)₂Br].H₂O}_n, consists of an one-dimensional polymeric chain which is perfectly linear and oriented along the y -axis. Within the polynuclear and polymeric complex, the Br atoms revealed their bridging properties forming two collinear bonds with two neighbouring Pt atoms. These Pt-Br bonds are much longer than those in the complex **1**, in which the coordination octahedrons are mutually separated [the Pt-Br bond distances are $2.455(3)$ and $2.8285(10) \text{ \AA}$ for **1** and **2**, respectively].

KRISTALNE STRUKTURE *TRANS,TRANS*-DIBROMOBIS(*N*-METILGLICINATO)PLATINA(IV) I NEOČEKIVANOG POLINUCLEARNOG KOMPLEKSA

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Reakcijom između K_2PtBr_6 i sarkozina a u prisustvu litijum hidroksida dobijeni su kristali dva kompleksa, *trans,trans*- $[Pt(Sar)_2Br_2]$ (**1**) i neočekivani polinuklearni $\{[Pt(SarH)_2Br] \cdot H_2O\}_n$ (**2**). Oba kompleksa platine su okarakterisani rendgenskom strukturnom analizom.

Eksperimentalni podaci su prikupljeni na difraktometru za monokristale uz korišćenje monohromatskog Mo- $K\alpha$ zračenja ($\lambda = 0.71069 \text{ \AA}$) i $\omega/2\theta$ skeniranja u opsegu θ ugla od 3.13 do 25.98° za kompleks **1** i od 2.40 do 25.96° za kompleks **2**. Za oba kompleksa je urađena korekcija za apsorpciju rendgenskog zračenja zasnovana na indeksiranju spoljnih plosni monokristala ($T_{min} = 0.0422$, $T_{max} = 0.3129$ za **1**; $T_{min} = 0.1261$, $T_{max} = 0.2442$ za **2**). Strukture su rešene metodom tetragornih atoma i diferentnom Furijeovom sintezom a utanjene su metodom najmanjih kvadrata pune matrice. Atomi vodonika su određeni geometrijski a utanjeni su uz vezivanje njihovih parametara za parametre odgovarajućih nevodoničnih atoma za koje su vezani kovalentnim vezama.

Kristalografski podaci za kompleks **1**: $C_6H_{12}Br_2N_2O_4Pt$, monoklinični sistem, prostorna grupa $P2_1/a$, $a = 10.921(8) \text{ \AA}$, $b = 9.562(3) \text{ \AA}$, $c = 6.890(5) \text{ \AA}$, $\beta = 125.46(5)^\circ$, $V = 585.5(6) \text{ \AA}^3$, $Z = 2$, $D_c = 3.012 \text{ g/cm}^3$, $\mu = 18.803 \text{ mm}^{-1}$, narandasti kristal sa dimenzijama $0.350 \times 0.300 \times 0.066 \text{ mm}$, $R_1 = 0.0711$ i $R_w = 0.1983$ ($GooF = 1.108$) za 72 utanjavana parametara i 869 refleksija sa $I > 2\sigma(I)$.

Kristalografski podaci za kompleks **2**: $C_6H_{12}BrN_2O_4Pt$, monoklinični sistem, prostorna grupa $C2/m$, $a = 12.362(5) \text{ \AA}$, $b = 5.657(2) \text{ \AA}$, $c = 9.616(4) \text{ \AA}$, $\beta = 118.00(3)^\circ$, $V = 593.8(4) \text{ \AA}^3$, $Z = 2$, $D_c = 2.613 \text{ g/cm}^3$, $\mu = 15.184 \text{ mm}^{-1}$, zeleni kristal sa dimenzijama $0.560 \times 0.014 \times 0.011 \text{ mm}$, $R_1 = 0.0426$ i $R_w = 0.1078$ ($GooF = 1.170$) za 51 utanjavana parametara i 643 refleksija sa $I > 2\sigma(I)$.

Kompleks **1** se sastoji od dve identične polovine vezane centrom simetrije. Oktaedarska koordinaciona geometrija je

značajno deformisana s obzirom da N-Pt-Br koordinacioni uglovi [84.1(4) i 95.9(4)°] izrazito odstupaju od očekivanih vrednosti od 90°.

Kompleks **2**, $\{[Pt(Sar-H)_2Br].H_2O\}_n$, se sastoji od jednodimenzionalnog polimernog lanca koji je idealno linearan i orjentisan duž y ose. Unutar ovog polinuklearnog i polimernog lanca atomi broma imaju ulogu mostnih liganada formirajući dve kolinearne veze sa dva susedna atoma platine. Ove Pt-Br veze su dosta duže nego (to je to slučaj u kompleksu **1** u kojem su koordinacioni poliedri odvojeni jedan od drugog [Dužine Pt-Br veza u kompleksima **1** i **2** su 2.455(3) i 2.8285(10) Å].

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