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XI КОНФЕРЕНЦИЈА
СРПСКОГ КРИСТАЛОГРАФСКОГ ДРУШТВА
Изводи радова

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CONTENT-САДРЖАЈ

ORAL PRESENTATIONS - САОПШТЕЊА

ORAL PRESENTATIONS

САОПШТЕЊА

STRONG METAL LIGAND AROMATIC CATION – π INTERACTIONS IN TETRAPHENYLBOREATE SALTS

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The cation – π interaction is considered to be an important non-covalent bonding force in a wide range of molecular systems. It was shown that this type of interactions can also exist when the cation is a transition metal complex [1]. Cation-π interactions between ligands coordinated to a metal cation and aromatic groups, metal ligand aromatic cation – π interactions (MLAC-π), have been found in crystal structures of metalloproteins from the Protein Data Bank [2] and as intramolecular interaction, in crystal structures of transition metal complexes from Cambridge Structural Database (CSD) [3].

Since in MLACπ interactions hydrogen atoms from ligands interact with π-systems, this interaction can be considered to be X-H…π bond. However, it is charge assisted bond since, by coordinating to the metal cation, ligands gain some positive charge. Here we report results of searching for intermolecular MLAC-π interactions between the hydrogen atom from a positively charged transition metal complex and phenyl groups from tetraphenylborate (TFB) anion. Since TFB is negatively charged it can be anticipated that this interactions can be relatively strong.

Screening the CSD provided over 200 structures in which an aromatic ring from TFB is close to a metal. We inspected these structures and selected 15 structures where the X…πc (πc - center of phenyl ring) distances were very short, and at the same time the X-H…πc angle was larger than 100^o. Based on the number of phenyl groups from the TFB anion interacting with the same ligand from metal complex, there are two types of intermolecular MLAC-π interactions. In the first type (I) two phenyl groups from TFB anion interact with the same ligand. In the second type (II) one aromatic group from the TFB anion interact with a ligand from transition metal complex.

[1] S. D. Zarić, *Chem. Phys. Lett.,* 311 (1999), 77.
[2] S. D. Zarić, D. M.Popović, E. W. Knapp, *Chemistry,* 6 (2000), 3935.
[3] M. K. Milčić, S. D. Zarić, *Eur.J.Inorg.Chem*., (2001), 2143.

JAKE METAL LIGAND AROMATSKE KATJON – π-INTERAKCIJE U SOLIMA SA TETRAFENILBORATNIM ANJONOM

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Katjon – π-interakcije se smatraju veoma bitnim nekovalantnimm vezivnim interakcijama u velikom broju molekulskih sistema. Pokazano je da te interakcije postoje i u sistemima u kojim je katjon kompleks prelaznog metala [1]. Katjon – π-interakcije izme|u liganada koordinovanih za metalni katjon i aromatičnih grupa, metal ligand aromatske katjon-π interakcije (MLAC-π), su pronađene u kristalnim strukturama metaloproteina iz proteinske banke podataka (PDB) [2] i, kao intremolekulske interakcije, u kristalnim strukturama kompleksa prelaznih metala iz Kembridžske banke kristalografskih podataka (CSD) [3].

Pošto u ovom tipu interakcija vodonikov atom sa liganda interaguje sa π-sistemom ove interakcije se mogu posmatrati kao X-H... π veza. Ova veza nastaje zbog toga što koordinacijom za centralni metalni jon, deo pozitivnog naelektrisanja prelazi sa metalnog jona na ligand. Ovde su izneti rezultati pretraživanja kristalografske banke podataka za intermolekulske MLAC-π interakcije između vodonikovog atoma sa pozitivno naelektrisanog kompleksa prelaznih metala i fenil grupe sa tetrafenilboratnog (TFB) anjona. Pošto je TFB negativno naelektrisan može se predpostaviti da će ove interakcije biti veoma jake.

Pretraživanjem banke kristalografskih podataka dobijeno je preko 200 struktura u kojima je aromatična grupa sa TFB anjona blizu metalnog jona. Sve ove strukture smo pobliže ispitali i odabrali njih 15 gde su X... πc (πc-centar benzenovog prstena) rastojanja veoma kratka, a u isto vreme ugao X-H... πc je veći od 100^o. Na osnovu broja fenil grupa sa TFB anjona koje interaguju sa istim ligandom sa metalnog kompleksa, postoje dva tipa intermolekulskih MLAC-π interakcija. U prvom tipu (I) ovih interakcija dve fenil grupe sa TFB anjona interaguju sa istim ligandom sa kompleksa prelaznog metala. U drugom tipu (II) samo jedna aromatična grupa sa TFB anjona interaguje sa jednim ligandom sa kompleksa prelaznog metala.

[1] S. D. Zarić, *Chem. Phys. Lett.*, 311 (1999), 77.
[2] S. D. Zarić, D. M. Popović, E. W. Knapp, *Chemistry,* 6 (2000), 3935.
[3] M. K. Milčić, S. D. Zarić, *Eur.J.Inorg.Chem.*, (2001), 2143.

STRUCTURE AND ELECTROSTATIC PROPERTIES OF A DECAVANADATE-CYTOSINE COMPLEX

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The polyoxometalates (POM's) of general formula $H_{6-x}A_xM_{10}O_{28}\cdot nH_2O$, ($A = K^+$, Na^+, M = W, V, n = 0-30) crystallize with a various number of water molecules. POM's primary structure is formed with polyanions while the secondary structure is formed with polyanions, cations and water molecules. POM's are studied for their potentially pharmaceutical applications (antiviral or antitumoral). These biological properties result from the POM's interactions with enzymes of cells at the nucleus membranes. The study of complex of POM's with amino acids or nucleic bases is therefore of a particular interest for a better understanding of their therapeutic impact.

Among the different synthesized POM's, we have focused on the polyoxovanadates (POV's). The vanadium has been chosen for its relative low toxicity in biological media compared for example to the tungstene. It has been established that, POV's are inhibitors or activators in the enzymatic reactions as kynase [1], phosphorilase [2] and ATP-ase of Ca^{2+} [2].

We are reporting the preliminary results of the electron density and the electrostatic properties of a decavanadate-cytosine complex of formula $Na_3V_{10}O_{28}(C_4N_3OH_5)_3(C_4N_3OH_6)_3\cdot 10H_2O$ (**1**). These properties are obtained from high resolution X-ray diffraction data (0.44 Å) at 210 K. **1** crystallizes in the $P\bar{1}$ space group, the crystallographic structure is also governed by interactions between the cytosine molecules which are protonated or not. The protonation-deprotonation process gives rise to additional diffraction peaks at temperature lower than 210 K. An instable $P\bar{1}$ to $P1$ phase transition was observed. Diffraction data have been refined using the Hansen-Coppens multipole model [3]. The electrostatic properties of the decavanadate-cytosine complex will be presented and discussed.

[1] D.W. Boyd, K. Kustin, M. Niwai, *Biochim. Biophys. Acta,* 827 (1985), 472.
[2] P. Csermely, A. Martonosi, G. C. Levy, A. J. Ejchart, *Biochem. J.,* 230 (1985), 807.
[3] N. Hansen and P. Coppens, *Acta Crystallogr.*, A34 (1978), 909.

STRUKTURA I ELEKTROSTATIČKE OSOBINE KOMPLEKSA DEKAVANADIJUM-CITOZINA

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Polioksometalati (POM) su jedinjenja opšte formule $H_{6-x}A_xM_{10}O_{28}\cdot nH_2O$, (A = K^+, Na^+, M = W, V, n = 0-30) koja kristališu sa različitim brojem molekula vode. Primarna struktura POM-a je sastavljena od polianjona dok je sekundarna struktura sastavljena od polianjona, katjona i molekula vode. POM-i su ispitivani zbog njihove potencijalne primene u farmaciji (anti-tumorna i anti-viralna aktivnost). Njihove biološke osobine su rezultat interakcije POM-a sa enzimima u membranama ćelijskog jezgra. Ispitivanje kompleksa POM-a sa amino kiselinama ili nukleinskim bazama je od ključnog interesa za bolje razumevanje njihovih terapeutskih dejstava.

Između različito sintetisanih POM-a, mi smo fokusirali naša ispitivanja na polioksovanadatima (POV). Vanadijum smo izabrali zbog relativno manje toksičnosti u biološkom medijumu u poređenu sa volframom. POV su inhibitori ili aktivatori u reakcijama enzima kao što su kinaze [1], fosforilaze [2] i ATP-aze [2].

Mi ćemo predstaviti preliminarne rezultate određivanja elektronske gustine kao i elektrostatičke osobine kompleksa dekavanadijum-citozina, formule $Na_3V_{10}O_{28}(C_4N_3OH_5)_3 (C_4N_3OH_6)_3 \cdot 10H_2O$ (**1**). Ovi rezultati su dobijeni na osnovu merenja visoke rezolucije (0.44 Å) intenziteta difrakcionih maksimuma sa monokristala na temperaturi od 210 K. Jedinjenje **1** kristalise u $P\bar{1}$ prostornoj grupi i njegova kristalna struktura je pod uticajem interakcija koje međusobno grade molekuli citozina. Na temperaturama nižim od 210 K je opažena pojava dodatnih difrakcionih maksimuma koji su posledica mogućnosti protonovanja i deprotonovanja molekula citozina. Opažen je nestabilan fazni prelaz iz prostorne grupe $P\bar{1}$ u $P1$. Difrakcioni podaci su utačnjeni uz korišćenje Hansen-Coppens multipol modela [1]. Elektostatičke osobine kompleksa dekavanadijum-citozina će biti prezentirane i diskutovane.

[1] D.W. Boyd, K. Kustin, M. Niwai, *Biochim. Biophys. Acta,* 827 (1985), 472.
[2] P. Csermely, A. Martonosi, G. C. Levy, A. J. Ejchart, *Biochem. J.,* 230 (1985), 807.
[3] N. Hansen and P. Coppens, *Acta Crystallogr.*, A34 (1978), 909.

SYNTHESIS AND CRYSTAL STRUCTURE OF TRIS[(1-PYRIDIN-2-YL-ETHYLIDENE)HYDRAZINE]IRON(II) PERCHLORATE

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The suspension of 0.42g (0.9 mmol) $Fe(ClO_4)_3 \cdot 6H_2O$ dissolved in 25 cm^3 water, 0.16g (1.35 mmol) dihydrazide oxalic acid and 0.33g (2.7 mmol) 2-acetylpyridine (molar ratio 2:3:6) together with 3 drops of $HClO_4$ ($c = 0.1$ mol/dm^3) was exposed to heating for 30 minutes, and dark-red microctystalline product was obtained in a yield of 45%.

During the coordination reaction, oxidative degradation of -CO-CO- side chain fragment and reduction Fe(III) to Fe(II) occurred. Besides that, a molecule of carbon-dioxide was obtained in the reaction. The structure of Fe(II) complex is given in a Figure 1.

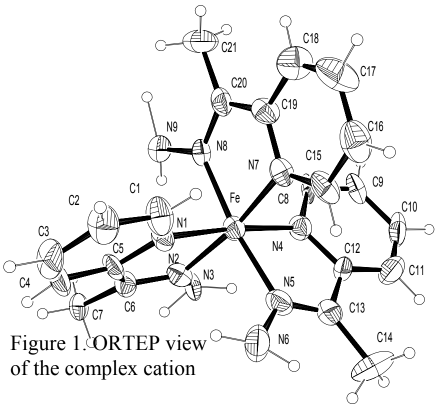

Figure 1. ORTEP view of the complex cation

Crystal data: $C_{21}H_{27}Cl_2FeN_9O_8$, $M_W = 660.27$, radiation MoKα, $\lambda = 0.71073$ Å, monoclinic, C2/c, $a = 36.023(5)$, $b = 14.349(3)$, $c = 10.612(2)$ Å, $\beta = 96.36(2)°$, $V = 5451.5(17)$ $Å^3$, $Z = 8$, Density (calculated) = 1.609 Mg/m^3, Reflections collected = 5735, Independent reflections = 3129 [R(int) = 0.1192], Data / restraints / parameters = 3129 / 5 / 393, Final R indices [$I > 2\sigma(I)$]: R1 = 0.0739, wR2 = 0.1658.

SINTEZA I KRISTALNA STRUKTURA TRIS[(1-PIRIDIN-2-IL-ETILIDEN)HIDRAZIN] GVOŽĐE(II) – PERHLORATA

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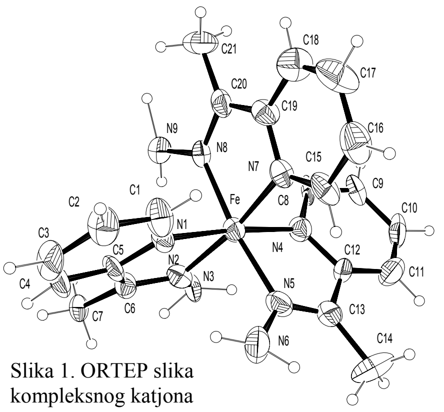
Polazeći od 0,42g (0,9 mmol) $Fe(ClO_4)_3 \cdot 6H_2O$ rastvorenog u 25 ml vode, 0,16g (1,35 mmol) dihidrazida oksalne kiseline i 0,33g (2,7 mmol) 2-acetilpiridina (molski odnos 2:3:6) uz dodatak 2-3 kapi $HClO_4$ (c = 0,1 mol/dm^3) pri zagrevanju na 65°C oko 30 minuta dobijen je tamnocrveni monokristalni proizvod u prinosu od 45 %.

U toku reakcije koordinovanja došlo je do oksidacione degradacije fragmenta bočnog lanca (-CO-CO-) i redukcije gvožđa(III) do gvožđa(II). Pri tome se iz sistema izdvojio ugljen dioksid. Dobijeni kompleks gvožđa(II) ima strukturu prikazanu na slici 1.



Slika 1. ORTEP slika kompleksnog katjona

Kristalografski podaci: $C_{21}H_{27}Cl_2FeN_9O_8$, $M_W = 660.27$, zračenje MoKα, $\lambda = 0,71073$ Å, monoklinični, C2/c, a = 36,023(5), b = 14,349(3), c = 10,612(2) Å, $\beta = 96,36(2)$ °, V = 5451,5(17) Å^3, Z = 8, gustina (izračunata) = 1,609 Mg/m^3, prikupljene refleksije: 5735, nezavisne refleksije: 3129 [R(int) = 0,1192], podaci / ograničenja / parametri = 3129 / 5 / 393, konačni R faktor [$I > 2\sigma(I)$]: R1 = 0,0739, wR2 = 0,1658.

ORIENTATION OF COORDINATED PYRIDINE IN CRYSTAL STRUCTURE OF COBALT(III) COMPLEX WITH SALICYLALDEHYDE S-METHYLISOTHIOSEMICARBAZONE

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Orientation of axially coordinated ligand can be very important in biomolecules. The orientation of histidines, axially ligated to heme, are considered to have influence on the function of heme cofactors in proteins. The orientation of histidines was studied by analyzing crystal structures of heme proteins [1] and by quantum chemical calculations [2]. It was shown that orientation of histidines is determined by interactions with side groups on porphirin.

The orientations of the pyridines in $[Co(L)(py)_3]I_3$ (H_2L = salicylaldehyde *S*-methylisothiosemicarbazone, py = pyridine) were studied by quantum chemical calculations [3]. Orientations of pyridines are caused by mutual influences of pyridines.

In this work we present the crystal structure of [Co(L)(bpy)(py)] (bpy = bipyridine) where coordination around Co(III) is distorted octahedral. Salicylaldehyde S-methylisothiosemicarbazone ligand is ONN-tridentate coordinated. Orientation of axially coordinated pyridine is different than in $[Co(L)(py)_3]I_3$ complex.

Crystallographic data: $C_{24}H_{24}CoI_3N_6OS$, triclinic crystal system, space group P-1, a = 9.990(3), b = 10.063(2), c = 14.739(3) Å, α = 96.063(6), β = 105.217(5), γ = 90.523(4) °, V = 1420.7(6) Å^3, Z = 2, F(000) = 840, D_c = 2.067 Mg/m^3, MoKα - radiation, μ(MoKα) = 3.966 mm^{-1}.

[1] S. D.Zarić, D. Popović, E. W. Knapp, *Biochemistry* 40 (2001), 7914-7928.
[2] V. B. Medaković, S. D. Zarić, *Inorg. Chim. Acta*, 349 (2003), 1-5.
[3] G. A. Bogdanović, V. B. Medaković, Lj. S. Vojinović, V. I. Češljević, V. M. Leovac, S. D. Zarić, *Polyhedron*, 20 (2001), 2231-2240.

ORIJENTACIJA KOORDINOVANOG PIRIDINA U KRISTALNOJ STRUKTURI KOMPLEKSA KOBALTA(III) SA S-METILIZOTIOSEMIKARBAZONOM SALICILALDEHIDA

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Orijentacija aksijalno koordinovanog liganda ima veoma važnu ulogu u biomolekulima. Orijentacija histidina, aksijalno vezanog za hem, jako utiče na funkciju kofaktora hema u proteinima. Orijentacija histidina proučavana je analizom kristalnih struktura proteina hema [1] i kvantno hemijskim proračunima [2]. Pokazano je da je orijentacija histidina određena interakcijama sa bočnim grupama iz porfirina.

Faktori koji utiču na orijentaciju koordinovanih piridina u $[Co(L)(py)_3]I_3$ (H_2L = *S*-metilizotiosemikarbazon salicilaldehida, py = piridin) proučavani su kvantno hemijskim metodama [3]. Orijentacije piridina uzrokovane su interakcijama između aksijalnih i ekvatorijalnog piridina.

U ovom radu predstavljena je kristalna struktura $[Co(L)(bpy)(py)]I_3$, (bpy = bipiridin) gde koordinacija oko Co(III) ima geometriju iskrivljenog oktaedra. *S*-metilizotiosemikarbazon salicilaldehida koordinovan je kao tridentatni ligand. Orijentacija aksijalno koordinovanog piridina razlikuje se od orijentacije u kompleksu $[Co(L)(py)_3]I_3$.

Kristalografski podaci: $C_{24}H_{24}CoI_3N_6OS$, triklinični kristalni sistem, prostorna grupa P-1, a = 9,990(3), b = 10,063(2), c = 14,739(3) Å, α = 96,063(6), β = 105,217(5), γ = = 90,523(4) °, V = 1420,7(6) $Å^3$, Z = 2, F(000) = 840, D_c = 2,067 Mg/m^3, MoKα - zračenje, μ(MoKα) = 3,966 mm^{-1}.

[1] S. D.Zarić, D. Popović, E. W. Knapp, *Biochemistry* 40 (2001), 7914-7928.
[2] V. B. Medaković, S. D. Zarić, *Inorg. Chim. Acta*, 349 (2003), 1-5.
[3] G. A. Bogdanović, V. B. Medaković, Lj. S. Vojinović, V. I. Češljević, V. M. Leovac, S. D. Zarić, *Polyhedron*, 20 (2001), 2231-2240.

A BINUCLEAR COBALT(II) COMPLEX CONTAINING PYROMELLITATE ION AND 1,10-PHENANTHROLINE

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Described compound presents continuation of our studies on ternary transition metal complexes containing anions of benzenepolycarboxylic acids and some aromatic diamines, as 1,10-phenathroline (phen) [1]. Due to the presence of four carboxylate groups, the tetraanion of 1,2,4,5-benzenetetracarboxylic (pyromellitic or pyr) acid can coordinate in numerous ways, acting as a bis monodentat [1] or polydentate [2,3] ligand having a bridging, chelating or combined function. In the polymeric complex $\{[Cu_2(pyr)(phen)_2]\cdot(H_2O)\}_n$, which has similar empirical formula to the title complex, pyr acts as tetradentate ligand and four COO groups are coordinated to four Cu atoms forming a double chain structure [3].

On the contrary, in our binuclear complex $[Co_2(pyr)(phen)_2(H_2O)_6]\cdot 2H_2O$, pyr is coordinated as bis-monodentate ligand. In addition, two *ortho*-COO groups are uncoordinated. The centre of symmetry is coinciding with the centre of aromatic ring. Co(II) environment consists of two N atoms (from phen) and four O atoms (three from H_2O molecules and one from COO group). The coordination polyhedron can be described as deformed octahedron with bond distances between 2.0550(19) and 2.1893(17) Å, and angles in the range 83.06(7) – 99.52(7) °.

Three coordinated H_2O molecules are the double donors in H bond network. One of them is the acceptor, too. The lattice H_2O molecule is an acceptor (toward O atom from one coordinated H_2O molecule) and donor (toward one O atom from uncoordinated COO group). There are four intramolecular H bonds, 2.588(3) and 2.714(2) Å, between coordinated H_2O and O atoms from COO groups.

Crystal data: $[Co_2(pyr)(phen)_2(H_2O)_6]\cdot 2H_2O$, $C_{34}H_{34}Co_2N_4O_{16}$, $M_r = 872.51$, triclinic, space group $P\overline{1}$, $a = 7.410(5)$, $b = 11.067(5)$, $c = 12.219(5)$ Å, $\alpha = 66.638(5)$, $\beta = 76.402(5)$, $\gamma = 70.855(5)$ °, $V = 862.61(8)$ Å^3, $Z = 1$, $F(000) = 448$, $\rho_x = 1.680$ g cm^{-3}, μ(Mo Kα) = 1.047 mm^{-1}, 4251 independent reflections, $R_1 = 3.29$ % for 3224 observed reflections with $I > 2\sigma(I)$, $R_{w2} = 7.17$ % (refinement on F^2) for all reflections and 285 refined parameters, with $(\Delta/\sigma)_{max} = 0.003$, $\Delta\rho_{max} = 0.323$ and $\Delta\rho_{min} = -0.286$ e Å^{-3}.

[1] D. Poleti, D. R. Stojaković, B. V. Prelesnik, R. M. Herak, *Acta Cryst.*, **C44** (1988), 242-245.
[2] R.-K. Chiang, N.-T. Chuang, Ch.-Sh. Wur, M.-F. Chong, Ch.-R. Lin, *J. Solid State Chem.*, **166** (2002), 158-163.
[3] Q. Shi, R. Cao, D.-F. Sun, M.-Ch. Hong, Y.-C. Liang, *Polyhedron*, **20** (2001), 3287-3293.

BINUKLEARNI KOBALT(II) KOMPLEKS SA PIROMELITAT JONOM I 1,10-FENANTROLINOM

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Opisano jedinjenje predstavlja nastavak naših istraživanja ternernih kompleksa prelaznih metala sa anjonima benzenpolikarboksilnih kiselina i nekih aromatičnih diamina, kao što je 1,10-fenatrolin (phen) [1]. Zbog prisustva četiri COO grupe, tetraanjon 1,2,4,5-benzentetrakarboksilne (piromelitne, pyr) kiseline može da se koordinira na brojne načine, ponašajući se kao bis monodentatni [1] ili polidentatni [2,3] ligand sa mostovnom, helatnom ili kombinovanom ulogom. U kompleksu $\{[Cu_2(pyr)(phen)_2]\cdot(H_2O)\}_n$, koji ima sličnu empirijsku formulu kao naše jedinjenje, pyr se ponaša kao tetradentatni ligand i četiri COO grupe su vezane za četiri Cu atoma gradeći dvostruke lance [3].

Suprotno ovome, u našem binuklearnom kompleksu, $[Co_2(pyr)(phen)_2(H_2O)_6]\cdot 2H_2O$, pyr je koordiniran kao bis-monodentatni ligand. Dodatno, dve orto-COO grupe su nekoordinirane. Centar simetrije se poklapa sa centrom aromatičnog prstena. Okruženje oko Co(II) čine dva N atoma (iz phen) i četiri O atoma (tri iz molekula H_2O i jedan iz COO grupe). Koordinacioni poliedar se može opisati kao deformisani oktaedar sa dužinama veza između 2,0550(19) i 2,1893(17) Å i uglovima u opsegu 83,06(7) – 99,52(7) °.

Tri koordinirana molekula H_2O su dupli donori vodonične veze, a jedan od njih je i akceptor. Voda kristalne rešetke je akceptor (preko O atoma iz jedne koordinirane H_2O) i donor (preko jednog O atoma iz nekoordinirane COO grupe). Postoje četiri intramolekulske vodonične veze, 2,588(3) i 2,714(2) Å, između koordiniranih H_2O i O atoma iz COO grupa.

Kristalografski podaci: $[Co_2(pyr)(phen)_2(H_2O)_6]\cdot 2H_2O$, $C_{34}H_{34}Co_2N_4O_{16}$, $M_r = 872,51$, triklinični sistem, prostorna grupa $P\bar{1}$, $a = 7,410(5)$, $b = 11,067(5)$, $c = 12,219(5)$ Å, $\alpha = 66,638(5)$, $\beta = 76,402(5)$, $\gamma = 70,855(5)$ °, $V = 862,61(8)$ Å^3, $Z = 1$, $F(000) = 448$, $\rho_x = 1,680$ g cm^{-3}, μ(Mo Kα) = 1,047 mm^{-1}, 4251 izmerenih refleksija, $R_1 = 3,29$ % za 3224 refleksija sa $I > 2\sigma(I)$, $R_{w2} = 7,17$ % (utačnjavanje pomoću F^2) za sve refleksije i 285 utačnjavanih parametara, sa $(\Delta/\sigma)_{max} = 0,003$, $\Delta\rho_{max} = 0,323$ i $\Delta\rho_{min} = -0,286$ e Å^{-3}.

[1] D. Poleti, D. R. Stojaković, B. V. Prelesnik, R. M. Herak, *Acta Cryst.*, **C44** (1988), 242-245.
[2] R.-K. Chiang, N.-T. Chuang, Ch.-Sh. Wur, M.-F. Chong, Ch.-R. Lin, *J. Solid State Chem.*, **166** (2002), 158-163.
[3] Q. Shi, R. Cao, D.-F. Sun, M.-Ch. Hong, Y.-C. Liang, *Polyhedron*, **20** (2001), 3287-3293.

CRYSTAL STRUCTURE OF A NEW NICKEL(II) COMPLEX CONTAINING PYROMELLITATE ION AND 2,2’-DIPYRIDYLAMINE

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The title binuclear complex, $[Ni_2(pyr)(dipya)_2(H_2O)_6]\cdot 4H_2O$, is a new example of ternary transition metal complexes containing tetraanion of pyromellitic (1,2,4,5-benzenetetracarboxylic) acid, pyr, and 2,2’-dipyridylamine, dipya, as aromatic diamine ligand. The interest in such complexes is related to the numerous possible coordination modes of pyr allowing interesting double chain [1] or 3-D network [2] structures.

The structure analysis showed that Ni atoms are in a deformed octahedral environment. The dipya is a usual chelating ligand, while the pyr anion acts as a bridge and it is coordinated in a bis-monodentate manner with two uncoordinated *ortho*-COO groups. Therefore, the pyr ligand behaves in fact as a terephthalato ligand. The three remaining apices in Ni(II) octahedron are occupied by three H_2O molecules. The bond distances in the octahedron are between 2.038(3) and 2.120(2) Å and angles in the range 83.58(9) – 95.56(10) °.

The binuclear coordination unit of the title compound is very similar to the recently obtained Co(II) complex $[Co_2(pyr)(phen)_2(H_2O)_6]\cdot 2H_2O$, phen = 1,10-phenanthroline.

Crystal packing is governed by a 3-D network of hydrogen bonds, which are in the range of 2.648(3) – 2.929(4) Å, and with O–H…O angles between 138.7(2) and 172.2(2) °. Four intramolecular H bonds between coordinated H_2O molecules and free O atoms from COO groups also exist.

Crystal data for $[Ni_2(pyr)(dipya)_2(H_2O)_6]\cdot 4H_2O$: $C_{30}H_{40}Ni_2N_6O_{18}$, $M_r = 890.10$, triclinic, space group $P\overline{1}$, $a = 9.3420(5)$, $b = 10.8890(5)$, $c = 12.0960(5)$ Å, $\alpha = 67.382(5)$, $\beta = 76.511(5)$, $\gamma = 84.395(5)$ °, $V = 1104.5(9)$ Å^3, $Z = 1$, $F(000) = 462$, $\rho_x = 1.338$ g cm^{-3}, μ(Mo Kα) = 0.925 mm^{-1}, $R_1 = 4.54$ % for 2721 observed reflections [$I > 2\sigma(I)$], $R_{w2} = 6.95$ % (refinement on F^2) for 4179 independent reflections and 253 refined parameters, with $(\Delta/\sigma)_{max} = 0.001$, $\Delta\rho_{max} = 0.640$ i $\Delta\rho_{min} = -0.445$ e Å^{-3}.

[1] Q. Shi, R. Cao, D.-F. Sun, M.-Ch. Hong, Y.-C. Liang, *Polyhedron*, **20 (**2001), 3287-3293.
[2] W. Chen, H. H. Tioh, J.-Z. Zou, Z. Xu, X.-Z. You, *Acta Cryst.*, **C52** (1996), 43-45; Ch.-D. Wu, C.-Zh. Lu, Sh.-F. Lu, H.-H. Zhuang, J.-Sh. Huang, *Inorg. Chem. Comm.*, **5** (2002), 171-174.

KRISTALNA STRUKTURA NOVOG NIKAL(II) KOMPLEKSA SA PIROMELITAT JONOM I 2,2'-DIPIRIDILAMINOM

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Navedeni binuklearni kompleks, $[Ni_2(pyr)(dipya)_2(H_2O)_6]\cdot 4H_2O$, je novi primer ternernog kompleksa prelaznih metala sa tetraanjonom piromelitne (1,2,4,5-benzentetrakarboksilne) kiseline, pyr, i 2,2'-dipiridilaminom, dipya, kao aromatičnim diaminskim ligandom. Interesovanje za ovakve komplekse potiče od brojnih mogućih načina koordinacije pyr koji dopuštaju zanimljive strukture dvostrukih lanaca [1] ili 3-D umrežene strukture [2].

Strukturna analiza je pokazala da su atomi Ni u deformisano oktaedarskom okruženju. Dipya je uobičajeno helatni ligand, dok se pyr anjon ponaša kao most i koordiniran je na bis-monodentatni način sa dve nekoordinirane orto-COO grupe. Tako se pyr ligand praktično ponaša kao tereftalato-ligand. Ostala tri roglja u Ni(II) oktaedru zauzimaju 3 molekula H_2O. Dužine veza u oktaedru su između 2,038(3) i 2,120(2) Å, a uglovi su u opsegu 83,58(9) – 95,56(10) °.

Binuklearna kompleksna jedinka navedenog kompleksa je vrlo slična ranije dobijenom Co(II) kompleksu $[Co_2(pyr)(phen)_2(H_2O)_6]\cdot 2H_2O$, phen = 1,10-fenatrolin.

Pakovanje kristala u molekulu određeno je 3-D sistemom vodoničnih veza koje su u opsegu 2,648(3) – 2,929(4) Å i sa O–H…O uglovima između 138,7(2) i 172,2(2) °. Takođe postoje četiri intramolekulske vodonične veze između koordiniranih molekula H_2O i slobodnih O atoma iz COO grupa.

Kristalografski podaci za $[Ni_2(pyr)(dipya)_2(H_2O)_6]\cdot 4H_2O$: $C_{30}H_{40}Ni_2N_6O_{18}$, $M_r = 890{,}10$, triklinični sistem, prostorna grupa $P\overline{1}$, $a = 9{,}3420(5)$, $b = 10{,}8890(5)$, $c = 12{,}0960(5)$ Å, $\alpha = 67{,}382(5)$, $\beta = 76{,}511(5)$, $\gamma = 84{,}395(5)$ °, $V = 1104{,}5(9)$ Å^3, $Z = 1$, $F(000) = 462$, $\rho_x = 1{,}338$ g cm^{-3}, μ(Mo Kα) = 0,925 mm^{-1}, $R_1 = 4{,}54$ % za 2721 refleksija $[I > 2\sigma(I)]$, $R_{w2} = 6{,}95$ % (utačnjavanje pomoću F^2) za 4179 izmerenih refleksija i 253 utačnjavanih parametara, sa $(\Delta/\sigma)_{max} = 0{,}001$, $\Delta\rho_{max} = 0{,}640$ i $\Delta\rho_{min} = -0{,}445$ e Å^{-3}.

[1] Q. Shi, R. Cao, D.-F. Sun, M.-Ch. Hong, Y.-C. Liang, *Polyhedron*, **20** (2001), 3287-3293.

[2] W. Chen, H. H. Tioh, J.-Z. Zou, Z. Xu, X.-Z. You, *Acta Cryst.*, **C52** (1996), 43-45; Ch.-D. Wu, C.-Zh. Lu, Sh.-F. Lu, H.-H. Zhuang, J.-Sh. Huang, *Inorg. Chem. Comm.*, **5** (2002), 171-174.

CRYSTAL STRUCTURE OF THE Ni(II) COMPLEX WITH S-METHYLISOTHIOSEMICARBAZIDE AND TEREPHTHALATE

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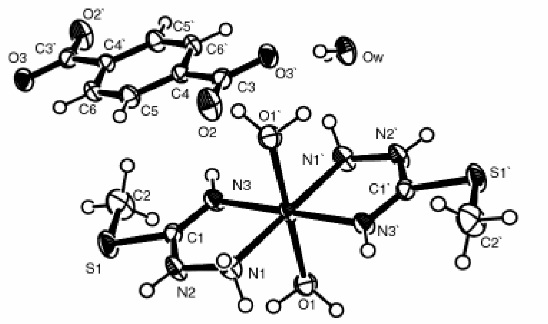

Crystallographic data: $C_{12}H_{25}N_6Ni_1O_8S_2$, monoclinic system, space group $P2_1/c$, a = 13.088(2), b = 5.653(1), c = 14.423(2) Å, β = 109.55(1)°, V = 1006.3(1) $Å^3$, Z = 2, D_c = 1.664 Mg/m^3, MoKα radiation, $\mu(MoK\alpha) = 1.23\ mm^{-1}$, Enraf-Nonius CAD-4 diffractometer. The structure was solved using SHELXS86 and refined using SHELXL97 programs to the final R faktor 0.0438 for 1368 independent reflections with $I>2\sigma(I)$ and 133 refined parameters.

The complex was obtained in the reaction of the aqueous solutions of $[NiL_2(NO_3)_2]$ (L = S-methylisothiosemicarbazide) and sodium-terephthalate. In the complex cation the nickel coordination geometry is distorted octahedral. The nickel atom and the terephthalate ring are positioned at symmetry centers. The crystal structure is stabilized by the complex hydrogen bonding network. The different coordination mode of S-metylisothiosemicarbazide relative to thiosemicarbazide, cause the distotrtion of the hydrogen bond motifs [1] usually present in the analogou complexes of thiosemicarbazide and N-substituted thiosemicarbazides [2].

[1] M. C. Etter, *J. Phys. Chem.*, 95, (1991), 4601-4610.

[2] M. T. Allen, A. D.Burrows, M. F. Mahon, *J. Chem. Soc. Dalton Trans.,* (1999), 215-221.

KRISTALNA STRUKTURA KOMPLEKSA Ni(II) SA S-METILIZOTIOSEMIKARBAZIDOM I TEREFTALATOM

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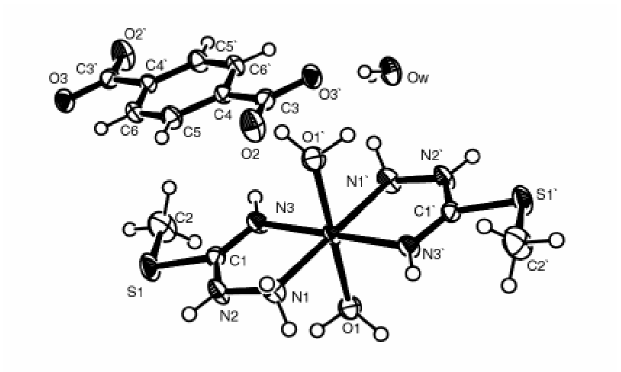

Kristalografski podaci: $C_{12}H_{25}N_6Ni_1O_8S_2$, monoklinični kristalni sistem, prostorna grupa $P2_1/c$, a = 13,088(2), b = 5,653(1), c = 14,423(2) Å, β = 109,55(1)°, V = 1006,3(1) $Å^3$, Z = 2, D_c = 1,664 Mg/m^3, MoKα zračenje, μ(MoKα) = 1,23 mm^{-1}, Enraf-Nonius CAD-4 difraktometar. Kristalna struktura je rešena korišćenjem programa SHELXS86 i utačnjena programom SHELXL97 do konačnog R faktora 0,0438 za 1368 nezavisnih refleksija sa $I>2\sigma(I)$ i 133 utačnjenih parametra.

Kompleks je sintetisan u reakciji vodenih rastvra $[NiL_2(NO_3)_2]$ (L = S-metilizotiose-mikarbazid) i natrijum–tereftalata. U kompleksnom katjonu atom nikla se nalazi u deformisanom oktaedarkom okruženju i zauzima centar inverzije. Tereftalatni prsten zauzima drugi centar inverzije. Kristalna struktura je stabilizovana složenim sitstemom vodoničnih veza. Razlika u koordinadiciji S-metilizotiosemikarbazida u odnosu na tiosemikarbazid uslovljava narušavanje karakterističnih motiva vodoničnih veza [1] prisutnih u analognim kompleksima tiosemikarabazida i N-metilovanih tiosemikarbazida [2].

[1] M. C. Etter, *J. Phys. Chem.*, 95 (1991), 4601-4610.
[2] M. T. Allen, A. D. Burrows, M. F Mahon, *J. Chem. Soc. Dalton Trans.*, (1999), 215-221.

ON THE FACTORS INFLUENCING THE INTERMOLECULAR CONTACTS BETWEEN THE COPPER(II) AND PHENYL RING IN THE SQUARE-PLANAR Cu(II) COMPLEXES

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There are few observations in the literature concerning the Cu(II)····C(phenyl) contacts at distances greater than 3.0 Å, and they have been disscused in terms of the bonding interaction between the copper atom and aromatic carbon. In a recent article [1] we have suggested that on the basis of the geometrical parameters and disposition of charges in the chelate and phenyl rings, this contact could be atributed to the interaction between the whole chelate ring and the phenyl fragment.

To obtain more insight into this type of interaction we have peformed the analysis of the geometrical parameters of the intermolecular Cu(II))····C(phenyl) contacts in the square-planar Cu(II) complexes. Results of this investigation will be presented and the factors which could possibly influence this interaction will be discusssed.

[1] Z. D. Tomić, V. M. Leovac, S. V. Pokorni, D. Zobel, S. D. Zarić, *Eur. J. Inorg. Chem.* (2003), 1222-1226.

FAKTORI KOJI UTIČU NA INTERMOLEKULSKE KONTAKTE IZMEDJU BAKRA(II) I FENILNOG PRSTENA KOD KVADRATNO-PLANARNIH Cu(II) KOMPLEKSA

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U literaturi se navodi nekoliko primera Cu(II)····C(fenil) kontakta na rastojanjima većim od 3.0 Å koji su razmatrani uz pretpostavku postojanja interakcije izmedju ova dva atoma. U našem prethodnom radu [1] ukazali smo da geometrijski parametri strukture bis[aceton-1-naftoilhidrazonato$^{(-1)}$]bakar(II) kompleksa, kao i raspodela naelektrisanja na atomima helatnog i fenilnog prstena sugerišu da u interakciji učestvuje na samo atom Cu već ceo helatni prsten.

Da bismo proverili osnovanost ovog zaključka izvršili smo analizu geometrijskih parametara koji opisuju Cu(II)····C(fenil) intermolekulske kontakte kod kvadratno planarnih Cu(II) kompleksa, uzimajući u obzir mogućnost da ovaj kontakt predstavlja helat-fenil interakciju. U radu će biti prikazani rezultati ove analize.

[1] Z. D. Tomić, V. M. Leovac, S. V. Pokorni, D. Zobel, S. D. Zarić, *Eur. J. Inorg. Chem.* (2003), 1222-1226.

CRYSTAL STRUCTURE OF POTASSIUM BIS(MALONATO)CUPRATE(II) DIHYDRATE

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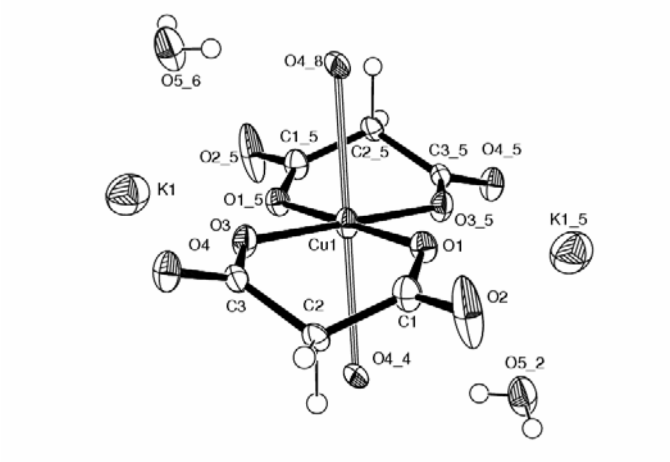
The light blue title compound was synthesised by the same procedure as for ethylenediammonium aquabis(malonato)oxovanadate(IV) [1].

Crystallographic data: $C_6H_8CuK_2O_{10}$, orthorhombic system, space group *Pbca*, *a* = 7.082(1), *b* = 9.402(1), *c* = 16.776(1) Å, V = 1117.0(2) Å^3, Z = 4, D$_c$ = 2.271 Mg/m^3, μ(Mo*Kα*) = 2.750 mm^{-1}, *F*(000) = 764. Data collection: 2.4 < θ < 26.0°, no. of parameters: 89, R = 0.0676, wR$_2$ = 0.2136 for 727 reflections with I>2σ(I).

The copper(II) is found in square-planar geometry surrounded by four carboxylate oxygen atoms from two malonato ligands. In axial position there are two carbonyl oxygen atoms, also from malonato ligands, at distance of 2.577 Å, forming distorted octahedron (angle O4–Cu–O4 180°). Around potassium atom there are six oxygen atoms, O1 and O3 which are coordinated to copper(II) ion, and O5 water molecule.



[1] G. N. Kaluđerović, F. W. Heinemann, V. M. Leovac, S. R Trifunović, T. J. Sabo, *Acta Cryst*. E59 (2003), m541-m542.

KRISTALNA STRUKTURA KALIJUM-BIS(MALONATO)KUPRAT(II) DIHIDRATA

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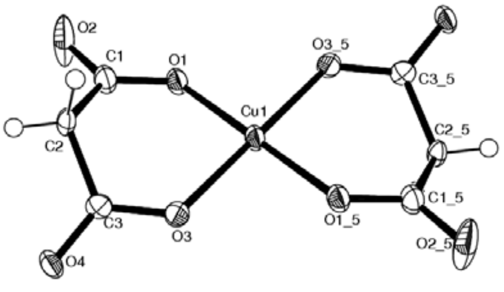
Svetlo plavi kompleks, $K_2[Cu(mal)]\cdot 2H_2O$ dobijen je po proceduri za etilendiammonium-akvabis(malonato)oksovanadat(IV) [1].

Kristalografski podaci: $C_6H_8CuK_2O_{10}$, ortorombični, prostorna grupa *Pbca* a = 7,082(1), b = 9,402(1), c = 16,776(1) Å, V = 1117,0(2) Å^3, Z = 4, D_c = 2,271 Mg/m^3, $\mu(MoK\alpha)$ = 2,750 mm^{-1}, $F(000)$ = 764. Opseg: $2,4 < \theta < 26,0°$, broj parametara: 89, R = 0,0676, wR_2 = 0,2136 za 727 refleksija sa $I>2\sigma(I)$.



Bakar(II) jon se nalazi u kvadratno planarnoj geometriji, okružen sa četiri karboksilna kiseonikova atoma malonato liganada. U aksijalnom položaju na rastojanju od 2,577 Å nalaze se O4 karbonilni kiseonikovi atomi gradeći deformisani oktaedar oko bakar(II) jona (ugao O4–Cu–O4 180°). Kalijum(I) jon se takođe nalazi u deformisanom oktaedarskom okruženju kiseonikovih atoma i to O1 i O3, karbonilni kiseonikovi atomi malonato liganda, i O5 molekul vode.

[1] G. N. Kaluđerović, F. W. Heinemann, V. M. Leovac, S. R Trifunović, T. J. Sabo, *Acta Cryst*. E59 (2003), m541-m542.

CRYSTAL STRUCTURE OF *TRANS*-DIBROMO(ETHYLENEDIAMINE-*N,N'*-DI-3-PROPIONATO)PLATINUM(IV) MONOHYDRATE

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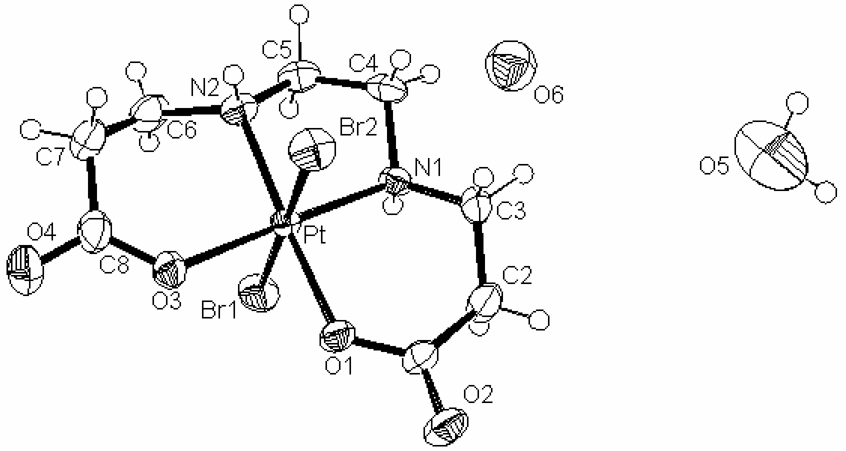
The title compound was synthesised by procedure for *trans*-dichloro(ethylenediamine-*N,N'*-di-3-propionato)platinum(IV) monohydrate [1]. The research of antitumor activity, for both complexes is in progress.



Crystallographic data: $PtC_8H_{16}Br_2N_2O_{5.16}$, monoclinic system, space group $P2_1/n$, a = 7.3575(8), b = 11.6720(14), c = 16.611(2) Å, β = 92.70(3)°, V = 1424.9(3) $Å^3$, Z = 4, D_c = 2.693 Mg/m^3, $\mu(MoK\alpha)$ = 1.547 mm^{-1}, F(000) = 1069. Data collection: $4.0 < \theta < 35.7°$, no. of parameters: 220, R = 0.0318, wR2 = 0.0619 for 4249 reflections with $I>2\sigma(I)$.

The platinum(IV) is hexacoordinated by two oxygen and two nitrogen atoms from eddp ligand, and two bromine atoms. It is expected that angles between Pt-Br bonds and coordinated atoms of eddp ligand are near 90°, but they show significant deviation. Namely, differences between N1-Pt-Br1 (87.6°) and N1-Pt-Br2 (94.2°) angles is about 7°. This can be explained by intramolecular interaction N1-H$\cdots$Br1 (H$\cdots$Br1 = 2.638 Å, angle N1-H$\cdots$Br1 = 114.5°) and N2-H$\cdots$Br2 (H$\cdots$Br2 = 2.667 Å, angle N2-H$\cdots$Br2 = 109.9°). Angle Br1-Pt-Br2 is 178.1°.

[1] G. N. Kaluđerović, G. A. Bogdanović, T. J. Sabo, *J. Coord. Chem.* 55 (2002) 817-822.

KRISTALNA STRUKTURA *TRANS*-DIBROMO(ETILENDIAMIN-*N,N’*--DI-3-PROPIONATO)PLATINA(IV) MONOHIDRATA

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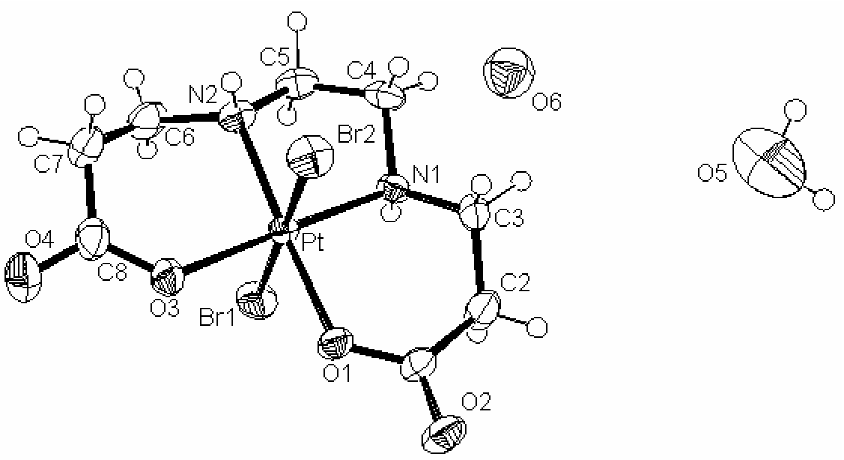
Kompleks *trans*-[Pt(eddp)Br_2] sintetisan je po postupku za dobijanje *trans*-(etilendiamin-*N,N’*-di-3-propionato)-dihloroplatina(IV) monohidrata [1] kao potencijalni antitumorski agens. Istraživanja aktivnosti oba kompleksa su u toku.



Kristalografski podaci: $PtC_8H_{16}Br_2N_2O_{5,16}$, monoklinični, prostorna grupa $P2_1/n$, a = 7,3575(8), b = 11,6720(14), c = 16,611(2) Å, β = 92,70(3)°, V = 1424,9(3) Å^3, Z = 4, D_c = 2,693 Mg/m^3, μ(Mo*Kα*) = 1,547 mm^{-1}, F(000) = 1069. Opseg: 4,0 < θ < 35,7°, broj parametara: 220, R = 0,0318, wR2 = 0,0619 za 4249 refleksija sa $I > 2\sigma(I)$.

Platina(IV) je heksakoordovana sa po dva atoma kiseonika i azota, iz *eddp* liganda, i dva atoma broma. Interesantno je da uglovi između Pt-Br veza i koordinovanih atoma *eddp* liganda pokazuju odstupanje od očekivanog ugla od 90°. Razlika između uglova N1-Pt-Br1 (87.6°) i N1-Pt-Br2 (94.2°) veća je od 7°. To se može objasniti intramolekulskim interakcijama: N1-H···Br1 (H···Br1 = 2,638 Å, N1-H···Br1 = 114,5°) i N2-H···Br2 (H···Br2 = 2,667 Å, N2-H···Br2 = 109,9°). Vrednost ugla Br1-Pt-Br2 je 178,1°.

[1] G. N. Kaluđerović, G. A. Bogdanović, T. J. Sabo, *J. Coord. Chem.* 55 (2002) 817-822.

SYNTHESIS AND CRUSTAL STRUCTURE OF $[Pt(terpy)(cyst\text{-}S)](ClO_4)_2{\cdot}0.5H_2O$

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The structure consists of discrete $[Pt(terpy)(cyst\text{-}S)]^{2+}$ cation and two perchlorate ions. Terpy is coordinated to platinum as a tridentate ligand and the fourth position is occupied by L-cysteine, which is coordinated via the sulfur atom. The coordination geometry around the platinum centre is distorted square-planar with N–Pt–N angles of 80.7(3), 80.5(3) and 161.1(3) °, and N–Pt–S angles of 99.8(2), 99.0(2) and 179.6(3) °. The Pt–N(2) distance to the central nitrogen atom of the terpy ligand, 1.982(7), is shorter than those to the other two nitrogen atoms of terpy, *viz.* 2.034(7) and 2.043(7) Å. The Pt–S distance is 2.304(3) Å. All these Pt–N and Pt–S bond distances, as well as bond distances and angles of terpyridine, compare well with those reported for the similar $[Pt(terpy)(thiourea)]^{2+}$ complex [1].

[1] Ž. D. Bugarčić, G. Liehr and R. van Eldik, *J. Chem. Soc., Dalton Trans.*, (2002), 2825 - 2830.

SINTEZA I KRISTALNA STRUKTURA $[Pt(terpy)(cyst\text{-}S)](ClO_4)_2\cdot 0.5H_2O$ KOMPLEKSA

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Određena je kristalna struktura kompleksa $[Pt(terpy)(cyst\text{-}S)]^{2+}$, gde je terpy 2,2’: 6’,2’’-terpiridin, a cyst-S je L-cistein. Struktura kompleksa je kvadratno-planarna. Terpi ligand je tridentatno koordinovana, a L-cistein je koordinovan preko sumpora. Dužina Pt–N(2) veze je 1,982(7) Å (to je centralni N atom iz terpi liganda) i ta veza je kraća od druge dve Pt–N veze, 2,034(7) i 2,043(7) Å. Veza Pt–S je 2,304(3) Å, što odgovara dužini drugih Pt–S veza u sličnim kompleksima [1]. Uglovi N–Pt–N su 80,7(3), 80,5(3) i 161,1(3), a N–Pt–S su 99,8(2), 99,0(2) i 179,6(3) °. Dužine veza i uglovi u koordinovanom terpi ligandu su slične odgovarajućim vezama u kompleksu $[Pt(terpy)(thiourea)]^{2+}$[1].

[1] Ž. D. Bugarčić, G. Liehr and R. van Eldik, *J. Chem. Soc., Dalton Trans.*, (2002), 2825 – 2830.

SYNTHESIS AND CRUSTAL STRUCTURE OF $[Pd(terpy)(py)](ClO_4)_2$

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The structure consists of discrete $[Pd(terpy)(py)]^{2+}$ cation and two perchlorate ions. The metal coordination sphere is square planar with expected deviations from right angles about Pd. The Pd–N bond length to the central atom of terpy ligand is well below 2.0 Å and it is significantly shorter than any of the other M–N distances (Table 1). The terpy ligand is almost coplanar with maximum displacement from the mean plane of –0.124(4) and +0.146(6) Å exhibited by N(1) and C(3), respectively. The pyridine forms a dihedral angle of 61.9(2) ° with the coordination N4 donors. These geometrical features are comparable to those observed in the related species containing methylcytosine [1].

The crystal packing evidences perchlorate anions located upper and below the metal (the shortest metal–oxygens contacts are about 3.48 Å), and the pyridine rings of centrosymmetric pairs of complexes that are marginally stacked, the shorter C–C distance being 3.5 Å.

Table 1. Selected bond distances (Å) and angles (°).

Pd–N(1)	2.039(4)	Pd–N(3)	2.038(4)
Pd–N(2)	1.932(4)	Pd–N(4)	2.038(4)
N(1) –Pd–N(2)	81.18(17)	N(2) –Pd–N(3)	80.72(17)
N(1) –Pd–N(3)	161.70(17)	N(2) –Pd–N(4)	177.48(16)
N(1) –Pd–N(4)	97.97(17)	N(3) –Pd–N(4)	100.22(16)

[1] S. Cosar, M. B. L. Janik, M. Flock, E. Freisinger, E. Farkas, B. Lippert, *J. Chem. Soc., Dalton Trans.*, (1999), 2329-2333.

SINTEZA I KRISTALNA STRUKTURA [Pd(terpy)(py)]$(ClO_4)_2$ KOMPLEKSA

B. Petrović[a], E. Zangrando[b] i Ž. D. Bugarčić,[a]

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Određena je struktura $[Pd(terpy)(py)]^{2+}$ kompleksa, gde je terpy 2,2’: 6’,2’’-terpiridin, a py je piridin. Kompleks je kvadratno-planaran. Terpi je tridentatno koordinovan, a četvrto mesto zauzima N iz piridina. Dužina Pd–N(2) veze (centralni atom N u terpi ligandu) je kraća od druge dve Pd–N veze, Tabela 1.

Table 1. Dužine veza (Å) i uglovi (°) u $[Pd(terpy)(py)]^{2+}$ kompleksu.

Pd–N(1)	2,039(4)	Pd–N(3)	2,038(4)
Pd–N(2)	1,932(4)	Pd–N(4)	2,038(4)
N(1)–Pd–N(2)	81,18(17)	N(2)–Pd–N(3)	80,72(17)
N(1)–Pd–N(3)	161,70(17)	N(2)–Pd–N(4)	177,48(16)
N(1)–Pd–N(4)	97,97(17)	N(3)–Pd–N(4)	100,22(16)

Dobijeni rezultati se mogu porediti sa ranije objavljenom strukturom paladijum kompleksa [1].

[1] S. Cosar, M. B. L. Janik, M. Flock, E. Freisinger, E. Farkas, B. Lippert, *J. Chem. Soc., Dalton Trans.*, (1999), 2329-2333.

$BaMgAs_2O_7$ AND $BaCoAs_2O_7$ – SYNTHESIS AND CRYSTAL STRUCTURES OF TWO NEW BARIUM DIARSENATES

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During work aimed at the hydrothermal preparation of synthetic members of the descloizite-adelite group, the title compounds were prepared by hydrothermal methods. Mixtures of $Ba(OH)_2$, $MgO/Co(OH)_2$, H_3AsO_4 and H_2O were transferred into teflon-lined stainless steal autoclaves and heated up to 493 K. The reactions were maintained under autogeneous pressure for three days followed by slow cooling to room temperature. The final products were filtered and washed thoroughly with distilled water. $BaMgAs_2O_7$ crystallised as transparent colourless prismatic crystals up to 0.15 mm in length and $BaCoAs_2O_7$ as transparent blue-green crystals up to 0.19 mm in length. These diarsenates represent two new members belonging to the $M1^{2+}M2^{2+}As_2O_7$ family of compounds.

Prior to our study, only five diarsenates with the general formula $M1^{2+}M2^{2+}As_2O_7$ were known [1]. Four of these ($PbCuAs_2O_7$, $BaCuAs_2O_7$, $SrCuAs_2O_7$ and $SrCoAs_2O_7$) crystallise in space group $P2_1/n$ with Z = 4, and the fifth one ($CaCuAs_2O_7$) crystallise in $P2_1/c$, but has different structure. The structures of these compounds consist of corner-sharing $M2O_5$ square pyramids and As_2O_7 diarsenate groups, where M1 atoms occupy the gap between two layer-like $[M2As_2O_7]$ units.

The structures of the title compounds were solved by direct methods [2] from single-crystal X-ray diffraction data (298 K, CCD detector, Mo$K\alpha$, $2\theta_{max} = 65°$) obtained from non-merohedrally twinned crystals [twin plane (100)]. The structure models were refined using SHELXL-97 [3]. The space group symmetry of both diarsenates is $P2_1/n$ with $Z = 4$. $BaMgAs_2O_7$ has $a = 5.620(1)$, $b = 8.629(2)$, $c = 13.344(3)$ Å, $\beta = 90.20(3)°$, $V = 647.1(2)$ Å^3 with $R_1 = 2.42$ % ($wR_2 = 5.26\%$) for 2349 unique reflections with, and $R_1 = 2.25\%$ for 2269 observed reflections using 102 free parameters. $BaCoAs_2O_7$ has $a = 5.651(1)$, $b = 8.580(2)$, $c = 13.282(3)$ Å, $\beta = 90.01(3)°$, $V = 664.0(2)$ Å^3 with $R_1 = 2.21\%$ ($wR_2 = 4.99\%$) for 2347 unique reflections with, and $R_1 = 2.09$ % for 2286 observed reflections using 102 free parameters. The structures are isotypic with the other $M1^{2+}M2^{2+}As_2O_7$ diarsenates crystallising in $P2_1/n$. The M2 position is five coordinated, which is rare coordination for Co and very rare for Mg.

Financial support of the Austrian Science Foundation (FWF) (Grant P15875-N03 to H. Effenberger) is gratefully acknowledged.

[1] T. C. Chen and S. L. Wang, *J. Solid State Chem.*, 121 (1996), pp 350-355.
[2] G. M. Sheldrick, SHELXS-97, a program for the solution of crystal structures. University of Göttingen, Germany (1997).
[3] G. M. Sheldrick, SHELXL-97, a program for crystal structure refinement. University of Göttingen, Germany (1997).

$BaMgAs_2O_7$ AND $BaCoAs_2O_7$ – SINTEZA I KRISTALNA STRUKTURA DVA NOVA DIARSENATA BARIJUMA

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U toku hidrotermalne sinteze novih sintetičkih članova grupe desklozit-adelit, kristalisali su novi diarsenati barijuma. Za sintezu je korišćena mešavina $Ba(OH)_2$, $MgO/Co(OH)_2$, H_3AsO_4 i H_2O tretirana u teflonima zagrevanim u anklavama od nerđajućeg čelika na 493 K. Reakcija se odigravala pod autogenim pritiskom 3 dana i praćena je sporim hlađenjem do sobne temperature. Finalni produkti su filtrirani i detaljno oprani destilovanom vodom. $BaMgAs_2O_7$ je iskristalisao kao providan, bezbojan, prizmatični kristal dužine do 0,15 mm, a $BaCoAs_2O_7$ kao providan, plavo-zeleni kristal dužine do 0,19 mm. Ovi diarsenati predstavljaju dva nova člana familije supstanci sa opštom formulom $M1^{2+}M2^{2+}As_2O_7$.

Do sada je bilo poznato samo pet $M1^{2+}M2^{2+}As_2O_7$ diarsenata [1]. Četiri od njih ($PbCuAs_2O_7$, $BaCuAs_2O_7$, $SrCuAs_2O_7$ i $SrCoAs_2O_7$) kristališu u prostornoj grupi $P2_1/n$ sa $Z = 4$, a peti ($CaCuAs_2O_7$) kristališe u $P2_1/c$ i pokazuje drugačiju strukturu. Struktura ovih stupstanci sastoji se od $M2O_5$-piramida povezanih rogljevima sa As_2O_7-diarsenat grupama i M1 atoma koji se nalaze u kanalima između dva sloja $[M2As_2O_7]$-jedinica.

Struktura diarsenata barijuma rešena je pomoću direktnih metoda [2] korišćenjem podataka dobijenih rendgenskom difrakcijom na monokristalu (298 K, CCD detektor, Mo$K\alpha$, $2\theta_{\max} = 65°$) i to nemerohedralno bližnjenih kristala [ravan bliznjenja je (100)] u oba slučaja]. Strukturni model utačnjavan je pomću SHELXL [3]. Oba diarsenata su utačnjena u prostornoj grupi $P2_1/n$ sa $Z = 4$. Parametri jedinične ćelije za $BaMgAs_2O_7$ su: $a = 5{,}620(1)$, $b = 8{,}629(2)$, $c = 13{,}344(3)$ Å, $\beta = 90{,}20(3)°$, $V = 647{,}1(2)$ Å^3, a $R_1 = 2{,}42\%$ ($wR_2 = 5{,}26\%$) za 2349 nezavisnih refleksija i $R_1 = 2{,}25\%$ za 2269 primećenih refleksija i 102 utačnjavana parametera. Parametri jedinične ćelije za $BaCoAs_2O_7$ iznose $a = 5{,}651(1)$, $b = 8{,}580(2)$, $c = 13{,}282(3)$ Å, $\beta = 90{,}01(3)°$, $V = 664{,}0(2)$ Å^3 sa $R_1 = 2{,}21\%$ ($wR_2 = 4{,}99\%$) za 2347 nezavisnih refleksija i $R_1 = 2{,}09\%$ za 2286 primećenih refleksija za 102 slobodno utačnjavana parametera. Oba barijum diarsenata su izostrukturna sa ostalim $M1^{2+}M2^{2+}As_2O_7$ diarsenatima koji kristališu u prostornoj grupi $P2_1/n$. Zanimljivo je napomenuti da M2 katjon kod $M1^{2+}M2^{2+}As_2O_7$ diarsenata pokazuje koordinaciju pet, što je retko okruženje za Co, a izuzetno retko okruženje za magnezijum.

Zahvaljujemo se Austrijskom fondu za nauku (FWF) (projekat P15875-N03 na ime H. Effenberger).

[1] T. C. Chen and S. L. Wang, *J. Solid State Chem.*, 121 (1996), pp 350-355.
[2] G. M. Sheldrick, SHELXS-97, a program for the solution of crystal structures. University of Göttingen, Germany (1997).
[3] G. M. Sheldrick, SHELXL-97, a program for crystal structure refinement. University of Göttingen, Germany (1997).

THE STATE OF ART AND EXPECTED DEVELOPMENTS ON THE CALIBRATION OF DIFFRACTOMETER

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The calibration of x-ray diffractometers implies to evaluate the residual systematic effects that are still present after the instrument alignment. When the alignment is performed as better as possible residual and not removable contributions to the diffraction pattern are present and their quantification possible. This evaluation is carried out by calculating the effective values of the parameters involved in the whole diffraction measurement process. These effective values are related to the actual experimental conditions, rather then the nominal values of the individual devices. The nominal values are provided by the manufacturers after the test on its site. The effective values of parameters involved in the diffraction experiment, and the effective functioning of the individual devices at the user site; these effective values enable the visualisation of "characteristic curves" of the diffraction measurements. When the uncertainty is associated to these curves, a reasonable confidence of the measurement reproducibility and repeatability may be reached.

The calibration process requires that the basic principle of the diffraction physics are considered. We report here the results obtained by using the Diffraction Instrumental Monitoring Methods and the protocol used by DISVAR96 package. In principle it can be extended to other packages and protocols useful for the diffraction pattern interpretation. Other developments are expected by extending the theory developed by Wilson [1]. This theory is in fact sometimes applied to divergent beams, where the gross effects (zero shift, divergence – axial and equatorial, specimen surface displacements) usually cover any other systematic effect. There are anyway some other secondary effects that become relevant when the gross effects are negligible as in the case of parallel beam geometry. These effects (lorentz, wavelength dispersion and even refraction) can contribute to the line position shift and the line broadening together other effects (2:1 misseting, inclination of the goniometer axis etc.).

One of the crucial points is the verification of the internal consistency of the parameters related to profile analysis of the diffraction lines. This internal consistency verification concerns the dependence on 2θ of the line position, the line broadening (FWHM), the mixing parameter (when the pseudo-Voigt is used) the normalised intensity. The fine analysis of this consistency requires that the verification will be extended to the asymmetric contribution to the diffraction line. When this asymmetric contribution can be analysed as a lorentzian addition to the profile analysis, the result is shown by the following Figures (Figs. 1 and 2).

The second crucial point is the horizontal and vertical balance of the table reporting the effective values of the individual devices contributing to the systematic effects. The vertical balance depends on individual diffractometers, the horizontal balance involves all the diffractometers participating to the calibration net.

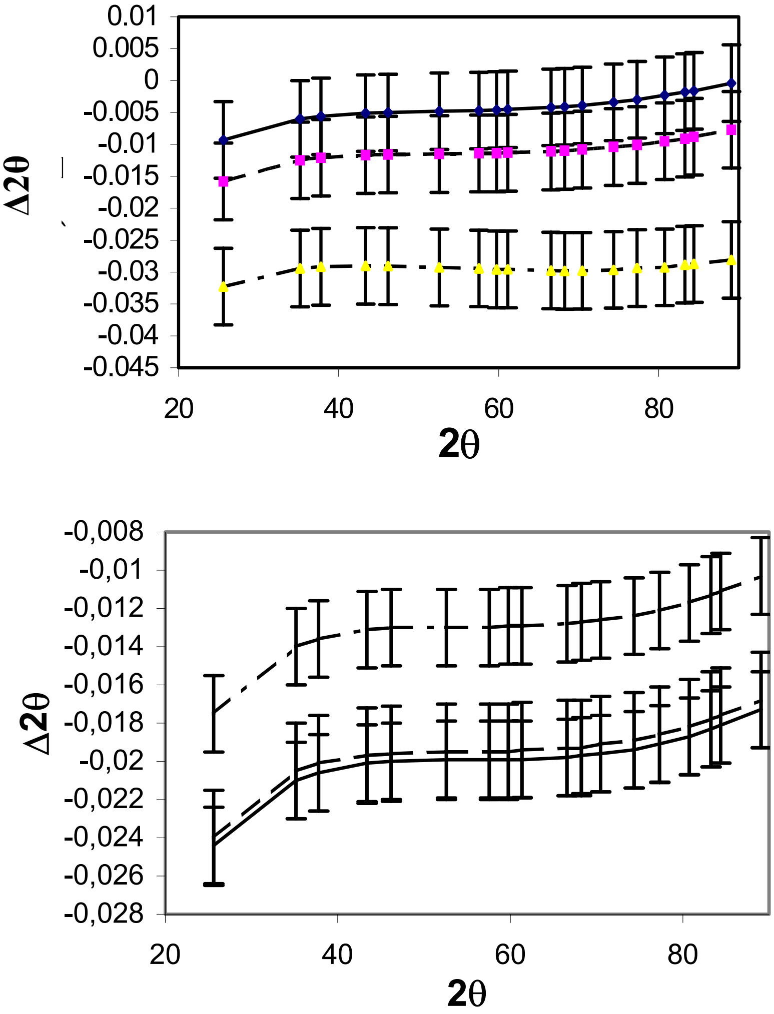
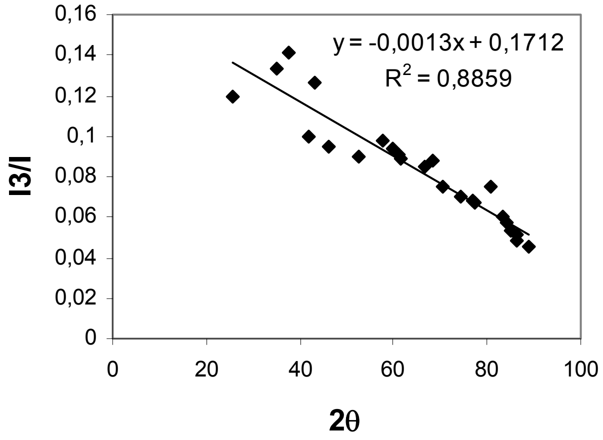


Figure 1. Characteristic curves with correspondent errors for the diffractometers A (up) and B (down); solid line (first cycle), dash line (second cycle) and dot-dash line (third cycle).



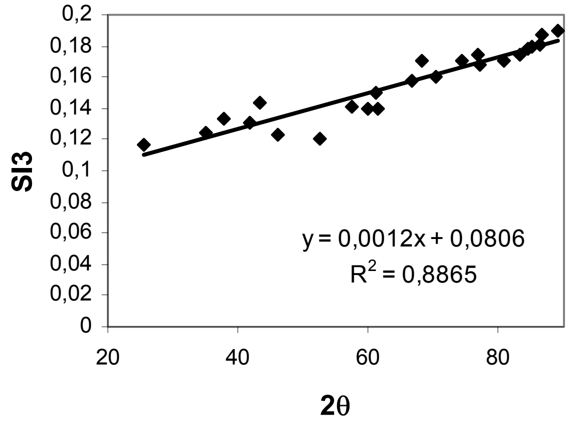


Figure 2. Evaluation of internal consistency of data for calibration purposes. When the Lorentzian function is used to represent the asymmetry the parameter I3 represents is intensity of the aberration and I is the intensity of the $CuK\alpha_1$ radiation. Si3 is the FWHM of asymmetry.

[1] A.J.C. Wilson (1963) “The Mathematical Theory of Powder Diffraction” Philips Technical Library.
[2] G. Berti, U. Bartoli, M. D’Acunto, F. De Marco, *Material Science Forum*, in press.
[3] G. Berti, *Powder Diffraction* 16 (2001), p. 1-5
[4] G. Berti, *Powder Diffraction*, 16 (2001), p. 6-15.

STRUCTURAL PROPERTIES OF $La_{1-x}Na_xMnO_3$ SOLID SOLUTIONS

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$La_{1-x}Na_xMnO_3$ ($x = 0$; 0.03; 0.06; 0.09; 0.12; 0.15) solid solutions were synthesized by ceramic technology.

The X-ray powder diffraction data were collected on a Philips PW1050 powder diffractometer with Ni-filtered CuK_α radiation. The data were collected in the 2θ region 10–110 °, with a step size of 0.02 ° and an exposure time of 10 s per step. The crystal structures were refined with the use of the Fullprof software package.

It was found that all samples crystallize in trigonal structure, in the space group R-3c. Also, it was found that after Glazer notation the configuration of oxygen octahedra belongs to $a^-a^-a^-$ type [1]. It is shown that the tilt angle between oxygen octahedra lies within 15-18 ° and it increases with the natrium content.

[1] A. M. Glazer, *Acta Cryst.*, B28 (1972), p. 3384-3392.

STRUKTURNE OSOBINE ČVRSTIH RASTVORA
$La_{1-x}Na_xMnO_3$

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Čvrsti rastvori $La_{1-x}Na_xMnO_3$ (x = 0, 0,03; 0,06; 0,09; 0,12; 0,15) sintetisani su klasičnom keramičkom tehnologijom.

Difraktogrami uzoraka snimljeni su na difraktometru za prah Philips PW1050 sa bakarnom anodom i Ni-filterom. Uzorci su snimani u intervalu 10 – 110 ° 2θ sa korakom od 0.02 ° i vremenom ekspozicije od 10 s. Za utačnjavanje kristalne strukture korišćen je program Fullprof.

Nadjeno je da svi uzorci kristališu u trigonalnoj prostornoj grupi R-3c, kao i da je konfiguracija zaokretanja kiseoničnih oktaedara u ovom slučaju tipa $a^-a^-a^-$ po Glazer-ovoj notaciji [1]. Pokazano je da se ugao zakretanja kiseoničnih oktaedara kreće od 15-18 ° i da se povećava sa koncentracijom natrijuma.

[1] A. M. Glazer, *Acta Cryst.*, B28 (1972), str. 3384-3392.

DETERMINATION OF MINERAL COMPOSITION OF URINARY CALCULI BY X-RAY POWDER DIFFRACTION ANALYSIS

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Urinary calculi are crystals formed mainly of one or more of the three components, oxalate (Whewellite - $CaC_2O_4{\cdot}H_2O$, Weddellite - $CaC_2O_4{\cdot}2H_2O$), phosphate (Hydroxylapatite - $Ca_5(PO_4)_3(OH)$, Whitlockite - $Ca_5(PO_4)_3$) and urate (Uricite - $C_4(NH)_2O_2C(NH)_2O$). These stones may contain various combination of cations, but the most common type of stone contains calcium in combination with either oxalate or phosphate. Cystine stones (*l*-Cystine - $C_6H_{12}N_2O_4S_2$) are less common. Urinary stones have become increasingly common in most parts of the world. [1]

The analysis of the urinary calculi only by chemical methods are rather unsatisfactory [2]. X-ray diffraction identifies the constituent of a calculus by their unique diffraction patterns, which allowes definite identification of an unknown crystalline substance. The mayor advantage of X-ray diffraction is it`s almost absolute identification of crystalline materials and mixtures of crystalline materials.

More then fifty samples of urocalculi from one of the Belgrade hospitals are investigated in this work. The results of X-ray diffraction analysis indicated that most of these samples belong to the oxalate and mixed type of oxalate-phosphate stones and represent up to 70 % of the investigated calculi. It has been shown that the mineral composition of the urocalculi relates to patient age.

[1] S. Nasir *et al.*, *Oxford Research Forum*, On-line journal., Art. 5.
[2] M. Daudon, R. J. Reveillaud, *Presse Med.*, (1987), Apr. 11, 16 (13), 627-631.

ОДРЕЂИВАЊЕ МИНЕРАЛНОГ САСТАВА УРИНАРНОГ КАМЕЊА МЕТОДОМ РЕНДГЕНСКЕ ДИФРАКЦИЈЕ ПРАХА

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Уринарно камење чине кристали настали углавном од једне или више компоненти: оксалата (вевелит - $CaC_2O_4 \cdot H_2O$, веделит - $CaC_2O_4 \cdot 2H_2O$), фосфата (хидроксиапатит - Ca5(PO4)3(OH), вајтлокит - $Ca_5(PO_4)_3$) и урата (урицит - $C_4(NH)_2O_2C(NH)_2O$). Могу да садрже разне катјоне, али најчешће садрже калцијум у комбинацији са оксалат- или фосфат-јонима. Камење изграђено од цистина (*l*-цистин - $C_6H_{12}N_2O_4S_2$) се ређе јавља. Појава уринарног камења је све заступљенија у многим деловима света [1].

Испитивање уринарног камења само хемијским методама често није задовољавајуће [2]. Дифракција рендгенских зрака идентификује минерални састав камена и обезбеђује потпуно дефинисање непознате кристалне супстанце. Основна предност примене методе рендгенске дифракције јесте у могућности идентификације како једне тако и мешавине више кристалних супстанци.

У овом раду испитано је више од 50 узорака уринарног камења пацијената из једне београдске болнице. Резултати рендгенских испитивања указују да већина узорака припада оксалатима или мешаном типу оксалат - фосфат, што представља више од 70 % испитиваних узорака. Показана је и зависност минералног састава уринарног камења у односу на старост пацијената.

[1] S. Nasir *et al.*, *Oxford Research Forum*, On-line journal., Art. 5.
[2] M. Daudon, R. J. Reveillaud, *Presse Med.*, (1987), Apr. 11, 16 (13), 627-631.

STRUCTURE AND MICROSTRUCTURE OF CATION DEFICIT Zn-Mn FERRITES

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The ultrafine $\mathrm{ZnFe_2O_4}$, $\mathrm{MnFe_2O_4}$ and cation deficit Zn-Mn ferrites were obtained by thermal decomposition of appropriate mixed complex compounds with acetylacetone(2,4–pentadione) ligands ($[\mathrm{M(AA)}_x]$) at 500 °C. In $\mathrm{ZnFe_2O_4}$ cation distribution is partial inverse, with about 20% of Zn^{2+} ions at octahedral *16d* sites, while $\mathrm{MnFe_2O_4}$ is a normal spinel. Cation distribution in nonstoichiometric $\mathrm{(Zn,Mn,Fe)}_{3-\delta}\mathrm{O}_4$ ($\delta \approx 0.28$-0.34) is found to be $(\mathrm{Zn}_x\mathrm{Mn}_y\square_\varepsilon)_{8a}[\mathrm{Fe}_z\square_\nu]_{16d}\mathrm{O}_4$, with a random distribution of vacancies. Nonstoichiometry in Zn-Mn ferrites is accompanied with the cation valence change, *i.e.* partial oxidation of Mn^{2+} to Mn^{4+}. Microstructure size-strain analysis [1,2] shows that the crystallite size decreases while crystallite strain increases with the Mn-concentration increase. Three-dimensional representation of crystallite size and strain by cubic harmonic function indicates that for $\mathrm{ZnFe_2O_4}$ average crystallite is in the "rhombohedron like" form while strains are higher in the crystal axes directions than between them. As the Mn-concentration increases this trend is less pronounced and three-dimensional body looks more like a spheroid.

[1] D. Balzar, *J. Res. Natl. Inst. Stand. Technol.*, **98** (1993), 321.
[2] J. Rodriguez-Carvajal, FullProf computer program, 1998, ftp://charybde.saclay.cea.fr/pub/divers/fullprof.98/windows/winfp98.zip

STRUKTURA I MIKROSTRUKTURA KATJONSKI DEFICITARNIH Zn-Mn FERITA

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Ultrafini prahovi $ZnFe_2O_4$, $MnFe_2O_4$ i katjonski deficitarnih Zn-Mn ferita dobijeni su termalnim razlaganjem odgovarajućih mešovitih kompleksnih jedinjenja sa acetilaceton(2,4–pentadion) ligandima ($[M(AA)_x]$) na 500 °C. Katjonska raspodela u $ZnFe_2O_4$ je delimično inverzna, sa oko 20% Zn^{2+} jona u oktaedarskim *16d* mestima, dok je $MnFe_2O_4$ spinel sa normalnom raspodelom katjona. Katjonska raspodela u nestehiometrijskim $(Zn,Mn,Fe)_{3-\delta}O_4$ ($\delta \approx 0.28\text{-}0.34$) je $(Zn_xMn_y\square_\varepsilon)_{8a}[Fe_z\square_\nu]_{16d}O_4$, sa slučajnom raspodelom vakancija ($\square$). Nestehiometrija u Zn-Mn feritima povezana je sa promenom valentnog stanja, tj. parcijalnom oksidacijom Mn^{2+} u Mn^{4+}. Analiza mikrostrukture [1,2] pokazuje da se dimenzija kristalita smanjuje a naprezanje u kristalitu povećava sa povećanjem koncentracije mangana. Trodimenzionalni prikaz kristalita i naprezanja u kristalitu za $ZnFe_2O_4$ pomoću kubne harmonijske funkcije ukazuje da je kristalit romboedarskog oblika i da je naprezanje izraženije u pravcu kristalografskih osa nego između njih. Sa povećanjem koncetracije mangana ovaj trend je sve manje izražen a trodimenzionalno telo sve više ima formu sferoida.

[1] D. Balzar, *J. Res. Natl. Inst. Stand. Technol.*, **98** (1993), 321.
[2] J. Rodriguez-Carvajal, FullProf computer program, 1998, ftp://charybde.saclay.cea.fr/pub/divers/fullprof.98/windows/winfp98.zip

MICROSTRUCTURE PARAMETERS OF Na – NEPHELINES WITH DIFFERENT Si/Al RATIO

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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 sodium and potassium. In nature, up to one quarter of those positions are occupied by potassium. 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 [1]. For these three samples microstructure parameters are calculated by the Warren – Averbach method, in order to obtain dependence between microstructure and Si/Al ratio. Results show increase of crystallite size and decrease of microstrain with disordering of framework cations.

[1] P. Vulić, R. Dimitrijević, V. Dondur, S. Macura, VIII Conference of the Serbian Crystallographic Society, Book of Abstracts, Kragujevac 2000, p. 77.

МИКРОСТРУКТУРНИ ПАРАМЕТРИ Na – НЕФЕЛИНА СА РАЗЛИЧИТИМ ОДНОСОМ Si/Al

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Нефелин (K,Na)$SiAlO_4$ је минерал из групе фелдспатоида. Његова структура може се извести из структуре тридимита, попуњавањем интерстицијских положаја натријумом и калијумом. У природном минералу калијум заузима до једне четвртине интерстицијских положаја. Применом термално индуковане трансформације зеолита раније су синтетизована три узорка натријумских нефелина. У складу са хемијским саставом 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 не-стехиометријска нефелина [1]. За сва три узорка одређени су микроструктурни параметри Warren – Averbach-овом методом, да би се успоставила зависност између микроструктуре и односа Si/Al. Резултати указују на повећање величине кристалита и смањење микронапрезања са смањењем уређености мрежних катјона.

[1] P. Vulić, R. Dimitrijević, V. Dondur, S. Macura, VIII Conference of the Serbian Crystallographic Society, Book of Abstracts, Kragujevac 2000, p. 77.

$2Bi_2O_3{\cdot}3TiO_2$ SYSTEM: STRUCTURAL CHANGES INDUCED BY INTENSIVE MILLING

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Previously, we have shown that mechanochemical treatment of either $2Bi_2O_3{\cdot}3TiO_2$ mixture or $Bi_4Ti_3O_{12}$ compound leads to a gradual formation of an amorphous phase, regardless of the initial state [1]. Here we report an attempt to derive relevant structural parameters: crystallite size, amount of amorphous phase and the transformed fraction (as a result of chemical reaction between Bi_2O_3 and TiO_2) of the powders milled for various milling times. The XRPD spectra are deconvoluted with the aid of Renex and PeakFit programs. The spectra were modelled as an amorphous halo plus a set of pseudo-Voigt peaks. The fraction of amorphous phase is estimated by the ratio of the integrated diffraction intensity of the amorphous halo to the total integrated diffraction intensity in the range 22.5–36.5 $^{o}2\theta$. For this procedure the calibration curve has been prepared using a series of mixtures of crystalline and "fully" amorphous $Bi_4Ti_3O_{12}$ powders in various proportions, *i.e.* 0, 20, 40, 50, 60, 80 and 100 wt.% of the crystalline phase.

The obtained structural parameters were used to follow kinetics of the processes taking place during mechanochemical treatment: crystallite size reduction, formation of amorphous phase and chemical reaction.

From such structural analysis it was concluded that amorphisation of the $Bi_4Ti_3O_{12}$ compound starts when crystallite size decreases to some critical value (bellow 400 Å). As the formation of amorphous phase proceeds, crystallite size further slightly decreases. In the Bi_2O_3–TiO_2 mixture, in which mechanically induced chemical reaction occurs, nanocrystalline $Bi_4Ti_3O_{12}$ was formed within the milling period up to 1 h. As chemical reaction continues, initially formed nanocrystalline phase transforms to the amorphous phase.

It was demonstrated that steady state (nanocrystalline/amorphous phase ratio) depends on milling conditions: higher milling intensity induces "nanocrystallisation" of amorphous phase, *i.e.* precipitation of crystallites with the average size of about 170 Å.

[1] M. Zdujić, Č. Jovalekić, Lj. Karanović, D. Poleti, X Conference of the Serbian Crystallographic Society, Book of Abstracts, Belgrade 2002, p. 37.

$2Bi_2O_3{\cdot}3TiO_2$ СИСТЕМ: СТРУКТУРНЕ ПРОМЕНЕ ИНДУКОВАНЕ ИНТЕНЗИВНИМ МЛЕВЕЊЕМ

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Раније је показано да механохемијски третман смеше састава $2Bi_2O_3{\cdot}3TiO_2$ или одговарајућег једињења $Bi_4Ti_3O_{12}$ води до постепеног образовања аморфне фазе, без обзира на различита почетна стања [1]. У овоме раду учињен је покушај да се у праховима млевеним разичито време одреде релевантни структурни параметри: величина кристалита, количина аморфне фазе и количина добијеног производа (као последице хемијске реакције између Bi_2O_3 и TiO_2). Извршена је деконволуција пикова на дифрактограмима прахова помоћу програма Renex и PeakFit. Спектри су описивани аморфним брегом и пиковима типа pseudo-Voigt. Удео аморфне фазе процењен је из односа интегралног дифрактованог интензитета аморфног брега према укупном интегралном дифрактованом интензитету у опсегу 22,5–36,5 $^{o}2\theta$. За ову сврху направљена је калибрациона крива од смеша кристалног и „потпуно“ аморфног праха $Bi_4Ti_3O_{12}$ разичитог састава и то: 0, 20, 40, 50, 60, 80 и 100 мас. % кристалне фазе.

Добијени структурни параметри коришћени су за праћење кинетике процеса који се одигравају током механохемијског третмана: смањење величине кристалита, образовање аморфне фазе и хемијска реакција.

Из ове структурне анализе закључено је да аморфизација $Bi_4Ti_3O_{12}$ једињења отпочиње тек након смањења кристалита до неке критичне величине (испод 400 Å). У наставку образовања аморфне фазе величина кристалита споро се смањује. У смеши Bi_2O_3–TiO_2 механички индукована хемијска реакција доводи до образовања нанокристалне $Bi_4Ti_3O_{12}$ фазе током периода млевења до 1 h. Даљим млевењем ова нанокристална фаза се трансформише у аморфну фазу.

Показано је да стационарно стање (однос нанокристална/аморфна фаза) зависи од услова млевења: већи интензитет млевења индукује „нанокристализацију“ аморфне фазе, тј. таложење (издвајање) кристалита величине од око 170 Å.

[1] М. Здујић, Ч. Јовалекић, Љ. Карановић, Д. Полети, X конференција српског кристалографског друштва, Књига извода радова, Београд, 2002. с. 38.

RADIAL DISTRIBUTION FUNCTION AND THE LOCAL STRUCTURE OF SOLID SOLUTIONS OF $Li_{0.5}Fe_{2.5-x}La_xO_4$ TYPE

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Within the framework of the systematic analysis of the structural properties of the solid solutions of $Li_{0.5}Fe_{2.5-x}La_xO_4$ type on the basis of the powder diffractograms, a calculation was performed of the radial density function (RAD) [1] for the basic ferrite (x=0) and two solid solutions with lantanas (x=0.1 and 0.05). These materials were synthesized by the procedure for obtaining nanoparticle samples [2] and powder diffractograms recorded with CuKα radiation indicated a possible presence of another phase.

The aim of these calculations was to demonstrate that one can notice the difference in the local structure of the solid solution by calculating PDF (pair distribution function), which is an average representation of the atomic ordering and provides the probability of finding certain atoms at a distance *r* from the referent atom [3]. PDF is the representation of diffraction data, obtained in this case from nanoparticle materials, in the real space where the distance between characteristic peaks represents the separation between the pairs of atoms. By calculating PDF from the model structure and comparing it with measured values, we can obtain the information about the local structure.

Calculated values of PDF function for three studied samples showed the difference in the positions of interatomic separations in the first and higher coordination spheres with a trend of increase of this difference for higher order neighbors.

Model structure can be established rather realistically since the crystal structure of Li-ferrite is refined by the Rietveld method in the space group $P4_332$. The structural study of nanoparticle solid solutions showed that the decrease of symmetry occurs and an eventual presence of another phase. These uncertainties of the structure justified the attempts of the analysis of the local structure with the aid of PDF function, as well as considering its possible advantages in the preliminary phase of the study of nanoparticle materials. Observed dependence of the structure of studied materials on sample preparation procedure is another reason to apply the proposed approach to such samples.

[1] V. Petkov, *J. Appl. Cryst.* 22 (1989), 387-389.
[2] R. G. Charel, M. A. Pawlikowski, *J. Phys. Chem.*, 62 (1958), 440.
[3] H. Klug, L. Alexander, X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials, Wiley, (1974), New York.

RADIJALNA FUNKCIJA RASPODELE I LOKALNA STRUKTURA ČVRSTIH RASTVORA TIPA $Li_{0.5}Fe_{2.5-x}La_xO_4$

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U okviru sistematske analize strukturnih osobina čvrstih rastvora $Li_{0.5}Fe_{2.5-x}La_xO_4$ tipa na bazi difraktograma praha urađeno je izračunavanje radijalne funkcije gustine (RAD) [1] za osnovni ferit (x=0) i dva čvrsta rastvora sa lantanom (x=0,1 i 0,05). Ovi materijali su sintetisani postupkom za dobijanje nanočestičnih uzoraka [2] i snimljeni difraktogrami praha korišćenjem CuKα zračenja, ukazivali su na moguće prisustvo druge faze.

Cilj ovih proračuna je bio da se pokaže da je moguće uočiti razliku u lokalnoj strukturi čvrstog rastvora izračunavanjem PDF (pair distributin function), koja daje prikaz srednjeg rasporeda atoma i daje verovatnoću nalaženja određenih atoma na rastojanju *r* od referentnog atoma [3]. PDF je prikaz difrakcionih podataka, u ovom slučaju dobijenih sa nanočestičnih materijala, u realnom prostoru gde rastojanje između karakterističnih pikova prikazuje razmak između parova atoma. Izračunavanjem PDF iz modelne strukture i poređenjem sa merenim vrednostima možemo dobiti informacije o lokalnoj strukturi.

Izračunate vrednosti PDF finkcije za tri ispitivana uzorka pokazala su razliku u položajima međuatomskih rastojanja u prvoj i višim koordinacionim sferama sa tendencijom povećanja te razlike za susede višeg reda.

Modelnu strukturu možemo dosta realno da postavimo jer je kristalna struktura Li-ferita utačnjena Ritveldovom metodom u prostornoj grupi $P4_332$. Strukturno ispitivanje nanočestičnih čvrstih rastvora pokazalo je da dolazi do sniženja simetrije i eventualno postojanje druge faze. Ove nedoumice u strukturi opravdale su pokušaje analize lokalne strukture preko PDF, kao i sagledavanje eventualnih prednosti ove analize u preliminarnoj fazi ispitivanja nanočestičnih materijala. Uočena zavisnost strukture ispitivanih materijala od postupka pripreme uzoraka još je jedan razlog da se predložena metoda primeni na ovakve uzorke.

[1] V. Petkov, *J. Appl. Cryst.* 22 (1989), 387-389.
[2] R. G. Charel, M. A. Pawlikowski, *J. Phys. Chem.*, 62 (1958), 440.
[3] H. Klug, L. Alexander, X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials, Wiley, (1974), New York.

NON-COVALENT INTERACTION IN CRYSTAL STRUCTURE OF E- AND Z- ISOMERS OF UNSATURATED ESTERS OF C-GLYCOSIDES

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The unsaturated esters of E- and Z- forms were prepared like as intermediate in the process of the syntheses of target C-nucleoside. The crystal and molecular structure were studied in previous contribution [1,2]. We describe here the crystal packing and the intermolecular interaction.

It was first noticed that **b** and **c** crystallographic axes are approximately doubled in Z-isomer, which increases the unit cell volume almost four times (V_1 = 665.98(4) Å^3, V_2=2610(1) Å^3) and changes the packing symmetry and the space group ($P1 \rightarrow P2_12_12_1$).

The basic difference between E (trans) and Z (cis) isomer in the crystalline form is in the creation of a new intramolecular hydrogen bond N5-H5…O1 (3.248(1) Å) in Z-isomer leading to the formation of new seven-member quasi ring. The rest of the molecule in both isomers retains the same conformation due to strong intramolecular hydrogen contacts in which the atom O16 is a fourfold acceptor of the hydrogen from the atoms C6, C7, C15 and C22. During the crystallization process, the change of the molecular conformation induces different packing and the change of the space group of the crystal unit cell. Relatively rigid conformation of the molecule except for the side chain at C4 atom, at the first step provide the packing of free molecules parallel to each other forming chains, with similar strong intermolecular hydrogen bonds in both isomers. In the second step, molecular chains bond mutually by relatively weak hydrogen bonds of C-H…O type, which vary in two studied isomers. It was observed that the acceptors of C-H…O contacts in this case are the peripheral oxygen atoms O9 and O30.

[1] A. Kapor, D. Zobel, M. Strümpel, Lj. Torović, M. Popsavin, Abstarcts, IX-Conference of the Serbian Crystallographic Society, (2001), 24-25
[2] A. Kapor, D. Zobel, M. Strümpel, Lj. Torović, M. Popsavin, Abstarcts, IX-Conference of the Serbian Crystallographic Society, (2002), 19-20

NEKOVALENTNE INTERAKCIJE U KRISTALNOJ STRUKTURI E- I Z- IZOMERA NEZASIĆENOG ESTRA C-GLUKOZIDA

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Nezasićeni estar E- i Z- forme je dobijen kao međuprodukt u procesu sinteze ciljnog C-nucleozida. Rešavanje kristalne i molekulske strukture ovih izomera je analizirano u prethodnim saopštenjima [1,2]. Ovde će biti opisano pakovanje molekula u kristalnoj rešetki kao i karakteristične intermolekularne interakcije.

Prvo je uočeno da se **b** i **c** kristalografske ose približno udvostručavaju u Z-izomeru, što povećava zapreminu elementarne ćelije četiri puta (V_1 = 665,98(4) $Å^3$, V_2 = 2610(1) $Å^3$) i menja simetriju pakovanja, odnosno prostornu grupu ($P1 \rightarrow P2_12_12_1$).

Osnovna razlika između E (trans) i Z (cis) izomera u kristalnoj formi je u nastanku nove unutar-molekulske vodonične veze N5-H5...O1 (3,248(1) Å) u Z-izomeru koja dovodi do formiranja novog sedmočlanog kvazi prstena. Ostatak molekula u oba izomera zadržava istu konformaciju zahvaljujući jakim unutar molekulskim vodoničnim kontaktima u kojima je atom O16 četvorostruki akceptor vodonika od atoma C6, C7, C15 i C22. U procesu kristalizacije izmena konformacije molekula uslovljava drugačije pakovanje i promenu prostorne grupe elementarne ćelije kristala. Relativno rigidna konformacija molekula, osim bočnog lanca na C4 atomu, u prvom koraku obezbeđuje pakovanje slobodnih molekula paralelno jedne drugima sa sličnim jakim međumolekulskim vodoničnim vezama u oba izomera. U drugom koraku ovako formirani lanci molekula se među sobom vezuju nešto slabijim vodoničnim vezama tipa C-H...O koje su različite u dva ispitivana izomera. Uočeno je da su akceptori C-H...O kontakata u ovom slučaju periferni atomi kiseonika O9 i O30.

[1] A. Kapor, D.Zobel, M.Strümpel, Lj.Torović, M.Popsavin, Abstarcts, IX-Conference of the Serbian Crystallographic Society, (2001), 24-25

[2] A. Kapor, D.Zobel, M.Strümpel, Lj.Torović, M.Popsavin, Abstarcts, IX-Conference of the Serbian Crystallographic Society, (2002), 19-20

THREE-DIMENSIONAL HYDROGEN-BONDING NETWORK IN THE CRYSTAL STRUCTURE OF PYRIDOXAL SEMICARBAZONE CHLORIDE MONOHYDRATE

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Crystal structure of pyridoxal semicarbazone chloride monohydrate, $C_9H_{13}N_4O_3{\cdot}Cl{\cdot}H_2O$, has been determined by single crystal X-ray analysis. Data were collected on an Enraf-Nonius CAD-4 diffractometer using Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å) and $\omega/2\theta$ scans in 2.13 to 26.96° θ range. Cell constants and an orientation matrix for data collection, obtained from 24 centered reflections in the θ range 12.30-15.61° corresponded to a triclinic system. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and difference-Fourier methods, and refined by full matrix least-squares using SHELXL97 program to a final R = 0.0635 for 1851 reflections with $I > 2\sigma(I)$. Water molecule and hydroxyl H-atom positions were determined by the HYDROGEN program [1] and were refined using a riding model with a fixed O-H bond length of 0.85 Å; isotropic displacement parameters of hydrogen atoms were set equal to 1.5 times the equivalent isotropic displacement parameter of the parent atoms.

All non-hydrogen atoms from the cation of pyridoxal semicarbazone (PxSC) are approximately coplanar. The presence of chloride anions and water molecules gives rise to an extensive hydrogen-bonded system. The crystal packing consists of parallel layers which are oriented in the direction of PxSC plane. These layers are interconected by hydrogen bonds through the Cl anions and water moleculs. Stereochemistry of presented crystal structure is compared to previously published structures of pyridoxal thiosemicarbazone trihydrate [2] and pyridoxal thiosemicarbazone cloride [3].

Crystallographic data: $C_9H_{15}ClN_4O_4$, triclinic, space group $P\bar{1}$, a = 7.163(2), b = 9.1320(10), c = 10.310(2) Å, α = 70.750(10), β = 77.49(2), γ = 81.462(10) °, V = 619.4(2) Å^3, Z = 2, D_c = 1.494 Mg/m^3, μ(Mo$K\alpha$) = 0.323 mm^{-1}, Mo$K\alpha$ radiation, λ = 0.71069 Å.

[1] M. Nardelli, *J. Appl. Cryst.*, 32 (1999) 563.
[2] U. Abram, K. Ortner, R. Gust, K. Sommer, *J.Chem.Soc., Dalton Trans.*, (2000) 735.
[3] M. F. Belicchi, G. F. Gasparri, E. Leporati, C. Pelizzi, P. Tarasconi, G. Tosi, *J.Chem.Soc., Dalton Trans.*, (1986) 2455.

TRODIMENZIONALNA MREŽA VODONIČNIH VEZA U KRISTALNOJ STRUKTURI PIRIDOKSAL-SEMIKARBAZON-HLORID-MONOHIDRATA

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Kristalna struktura piridoksal-semikarbazon-hlorid-monohidrata, $C_9H_{13}N_4O_3{\cdot}Cl{\cdot}H_2O$, određena je rendgenskom strukturnom analizom. Eksperimentalni podaci su prikupljeni na difraktometru uz korišćenje monohromatskog Mo$K\alpha$ zračenja (λ = 0,71069 Å) i $\omega/2\theta$ skeniranja u opsegu θ ugla od 2,13 do 26,96°. Dimenzije jedinične ćelije i orijentaciona matrica dobijeni su korišćenjem 24 centriranih refleksija koje su bile u opsegu θ ugla od 12,30-15,61° i odgovarale su trikliničnom sistemu. Podaci su korigovani na Lorencov i polarizacioni faktor. Struktura je rešena direktnim metodama i diferentnom Furijeovom sintezom a utačnjena je metodom najmanjih kvadrata pune matrice korišćenjem programa SHELXL97 do finalnog R = 0,0635 za 1851 refleksija koje zadovoljavaju uslov $I > 2\sigma(I)$. Atomi vodonika iz molekula vode i hidroksilnih grupa određeni su korišćenjem programa HYDROGEN [1], a utačnjeni su sa fiksiranim dužinama O–H veza u vrednosti od 0,85 Å. Izotropni temperaturni faktori ovih atoma vodonika fiksirani su na vrednost 1,5 puta veću od vrednosti ekvivalentnih izotropnih parametara nevodonikovih atoma za koje su vezani.

Svi nevodonikovi atomi iz katjona piridoksal-semikarbazona (PxSC) su približno koplanarni. Prisustvo anjona hlora i molekula vode omogućilo je građenje sistema vodoničnih veza. Kristalno pakovanje se sastoji od paralelnih slojeva orjentisanih u pravcu pružanja PxSC-ravni. Ovi slojevi su međusobno povezani građenjem vodoničnih veza preko anjona hlora i molekula vode. Stereohemija prezentovane kristalne strukture upoređena je sa prethodno publikovanim strukturama piridoksal-tiosemikarbazon-trihidrata [2] i piridoksal-tiosemikarbazon-hlorida [3].

Kristalografski podaci: $C_9H_{15}ClN_4O_4$, triklinični sistem, prostorna grupa $P\bar{1}$, a = 7,163(2), b = 9,1320(10), c = 10,310(2) Å, α = 70,750(10), β = 77,49(2), γ = 81,462(10) °, V = 619,4(2) Å^3, Z = 2, D_c = 1,494 Mg/m^3, μ(Mo$K\alpha$) = 0,323 mm^{-1}, Mo$K\alpha$ zračenje, λ = 0,71069 Å.

[1] M. Nardelli, *J. Appl. Cryst.*, 32 (1999) 563.
[2] U. Abram, K. Ortner, R. Gust, K. Sommer, *J.Chem.Soc., Dalton Trans.*, (2000) 735.
[3] M. F. Belicchi, G. F. Gasparri, E. Leporati, C. Pelizzi, P. Tarasconi, G. Tosi, *J.Chem.Soc., Dalton Trans.*, (1986) 2455.

SYNTHESIS AND CRYSTAL STRUCTURE OF 3,16,17-TRIHYDROXY-16,17-SECOESTRA-1,3,5(10)-TRIENE

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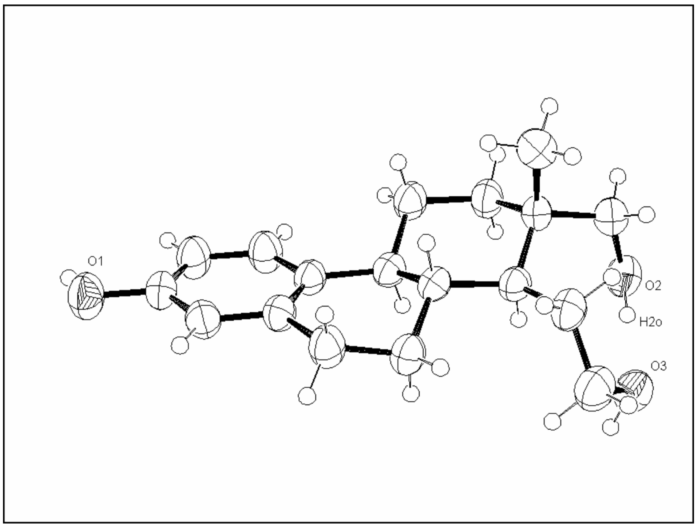
In order to study estrogenic vs. antiestrogenic activity, a new compound, 3,16,17-trihydroxy-16,17-secoestra-1,3,5(10)-triene, was synthesized in several synthetic steps starting from estrone.

The compound crystallyzes in the orthorhombic system, space group $P2_12_12_1$, with the unit cell parameters a = 10.195(5), b = 6.675(5), c = 23.145(5) Å, Z = 4, $D_x = 1.225$ M gm^{-3}, $\mu = 0.08$ mm^{-1}, MoK$_\alpha$ radiation.

The crystal structure was solved by direct methods on the basis of 2515 indipendent reflections using SHELXS-97 [1] and refined by SHELXL-97 [1]. The final R factor is 0.0216 for 1027 reflections with $I > 2\sigma(I)$.



Perspective view of the molecule

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

SINTEZA I KRISTALNA STRUKTURA 3,16,17-TRIHIDROKSI-16,17-SEKOESTRA-1,3,5,(10)-TRIENA

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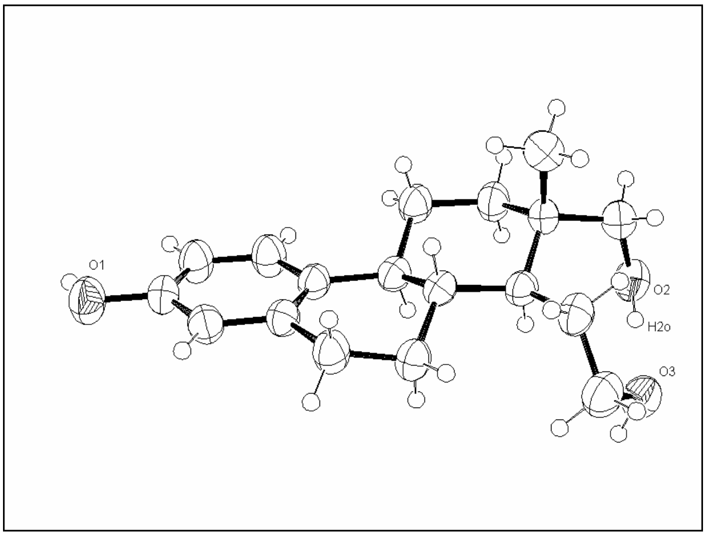
U cilju ispitivanja estrogene odnosno antiestrogene aktivnosti, polazeći od estrona, sintetizaovano je u više sintetskih faza novo jedinjenje:
3,16,17-trihidroksi-16,17seko-estra-1,3,5(10)-trien.

Jedinjenje kristališe u ortorombičnom kristalografskom sistemu, prostorna grupa $P2_12_12_1$, sa parametrima elementarne ćelije a = 10,195(5), b = 6,675(5), c = 23,145(5) Å, Z = 4, D_x = 1,225 Mg m^{-3}, μ = 0,08 mm^{-1}, MoK_α zračenje.

Struktura kristala rešena je primenom direktnih metoda na bazi 2515 nezavisnih refleksa pomoću SHELXS-97 [1] i utačnjena pomoću SHELXL-97 [1]. Konačna vrednost R-faktora je 0,0216 za 1027 refleksa sa I > 2σ(I).



Trodimenzionalni prikaz molekula

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

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CRYSTAL STRUCTURE AND THE INFLUENCE OF NEW 3,17-SUBSTITUED D-SECO-ESTRONE DERIVATIVES ONTO THE PHYSICAL CHARACTERISTICS OF THE BINARY MIXTURES OF THE CHOLESTERIC LIQUID CRYSTALS

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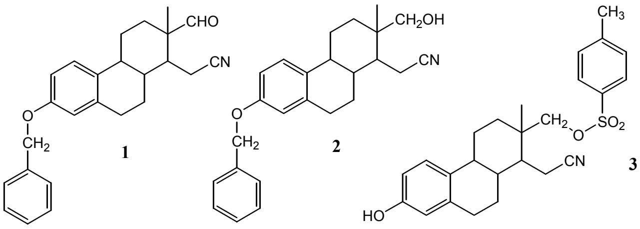
The crystal structure and influence of the new chiral additives, potential antiestrogenes, onto the physical characteristics of the binary mixtures of cholesteric liquid crystals were studied. The tested D-seco-estratriene-derivatives **1**-**3** (3-benzyloxy-17-oxo-16,17-secoestra-1,3,5(10)-triene-16-nitrile, **1**; 3-benzyloxy-17-hydroxy-16,17-secoestra-1,3,5(10)-triene-16-nitrile, **2** and 3-hydroxy-17-*p*-toluenesulphonyloxy-16,17-secoestra-1,3,5(10)-triene-16-nitrile, **3**) were synthesized in several synthetic steps, starting from estrone.



1 **2** **3**

The phase transitions of the mixture of cholesteryl laurate and cholesteryl enantate with the added chiral additives **1-3** (45%-45%-10%; **Mix1**, **Mix2** and **Mix3**, respectively) were examined. A considerable shift of the phase transition temperature I→Ch, as well as the temperature of the SmA phase formation was observed. X-ray diffraction data enabled the determination of the crystal and molecular structure of the compound **3** and its molecular length (l) and width (d*), as well as the molecular parameters of the mixtures **Mix1, Mix2** and **Mix3**: the thickness of smectic *i.e.* long spacing distance of cholesteric layers (d) and average distance between the long axes of neighbouring molecules (D). The most probably conformation of the compounds **1**, **2** were determined by the molecular-mechanic calculations on the basis of solved crystal structure. The influence of these chiral additives onto the pitch of the cholesteric helix of the studied binary mixtures of the cholesteric liquid crystals was also investigated.

KRISTALNA STRUKTURA I UTICAJ NOVIH 3,17-SUPSTITUISANIH D-SEKO-ESTRONSKIH DERIVATA NA FIZIČKE KARAKTERISTIKE BINARNIH SMEŠA HOLESTERIČKIH TEČNIH KRISTALA

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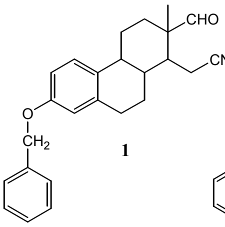
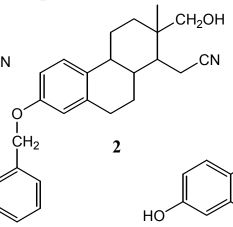
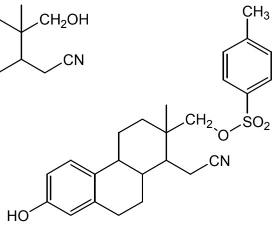
Određena je kristalna struktura i ispitivan uticaj novih hiralnih aditiva, potencijalnih antiestrogena, na fizičke karakteristike binarnih smeša holesteričkih tečnih kristala. Ispitivani D-seko-estratrienski derivati **1**-**3** (3-benziloksi-17-okso-16,17-sekoestra-1,3,5(10)-trien-16-nitril, **1**; 3-benziloksi-17-hidroksi-16,17-sekoestra-1,3,5(10)-trien-16-nitril, **2** i 3-hidroksi-17-*p*-toluensulfoniloksi-16,17-sekoestra-1,3,5(10)-trien-16-nitril, **3**) sintetisani su u nekoliko sintetskih faza, polazeći od estrona.



1



2



3

Ispitivani su fazni prelazi smeša holesteril laurata i holesteril enantata prilikom dodavanja hiralnih aditiva **1-3** (45%-45%-10%; **Mix1, Mix2** and **Mix3**, respektivno). Primećen je značajan pomak temperature faznog prelaza I→Ch, kao i temperature formiranja SmA faze. Podaci dobijeni difrakcijom x-zraka omogućili su određivanje kristalne i molekulske strukure, tj. dužine (l) i širine (d*) molekula jedinjenja **3**, kao i molekulskih parametara smeša **Mix1, Mix2** i **Mix3**: debljine smektičkih slojeva, odnosno uređenja na daljinu holesteričkih slojeva (d) i srednje vrednosti rastojanja između dugih osa susednih molekula (D). Najverovatnija konformacija jedinjenja **1** i **2** je određena pomoću molekularno-mehaničkih proračuna na bazi kristalne strukture jedinjenja **3**. Takođe je ispitivan uticaj hiralnih aditiva na promenu koraka holesteričke spirale binarnih smeša holesteričkih tečnih kristala.

SYNTHESIS AND CRYSTAL STRUCTURE INVESTIGATIONS OF TWO ANDROSTENE DERIVATIVES

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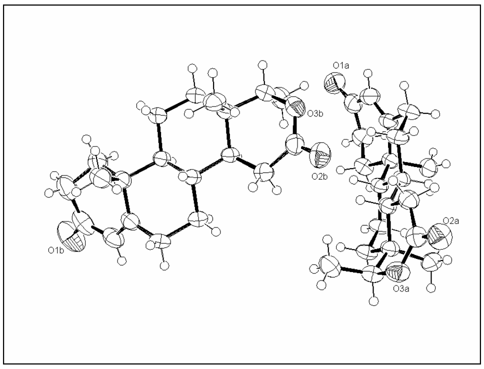
17aα-methyl-17-oxa-D-homo-4-androstene-3,16-dione **(1)** and 17aα-methyl-17-oxa-D-homo-1,4,6-androstatrien-3,16-dione **(2)** were synthesized from 3β-hydroxy-16-oximino-5-androstene-17-one in several synthetic steps.

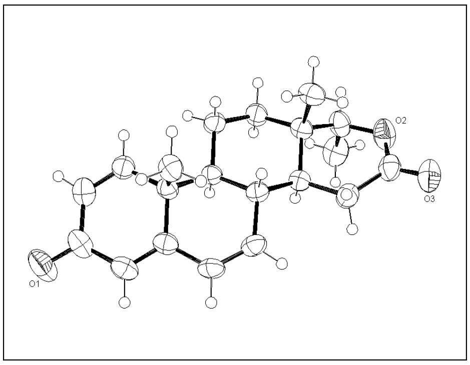
The compound **1** crystallizes in the triclinic system, space group P1, with the unit cell parameters a=8.040(2), b=8.160(2), c=13.658(7) Å; α=77.03(3), β=88.95(3), γ=89.22(2) °, V=854.95(8) Å^3, Z=2, D_x=1.229 M gm^{-3}, μ=0.08 mm^{-1}, MoKα radiation.

The compound **2** crystallizes in the orthorhombic system, space group $P2_12_12_1$, with the unit cell parameters a=7.225(2), b=8.887(2), c=25.358(8) Å, V=1628.2(2) Å^3, Z=4, D_x=1.270 M gm^{-3}, μ=0.08 mm^{-1}, MoKα radiation.

Both structures were solved by direct methods using SHELXS-97 [1], and refined by SHELXL-97 [1]. The final R factors for compounds **1** and **2** are 0.0486 (for 3683 reflections with I>2σ(I)) and 0.0427 (for 1547 reflections with I>2σ(I)), respectively.



Perspective view of the molecule **1**



Perspective view of the molecule **2**

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

SINTEZA, STRUKTURNA I KRISTALOGRAFSKA ISTRAŽIVANJA DVA DERIVATA ANDROSTENA

O. Klisurić[a], **S. Stanković**[a], **D. Lazar**[a], **D. Zobel**[b], **K. Penov-Gaši**[a], **S. Stajanović**[a]

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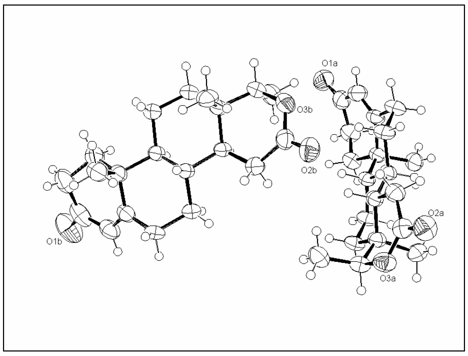
17aα-metil-17-oksa-D-homo-4-androsten-3,16-dion **(1)** i 17aα-metil-17-oksa-D-homo-1,4,6-androstrien-3,16-dione **(2)** su sintetizovani polazeći od 3β-hidroksi-16-oksimino-5-androsten-17-ona u nekoliko sintetskih faza.

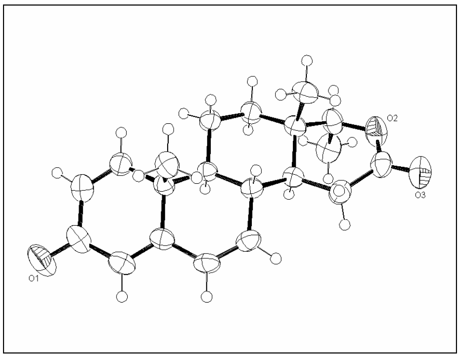
Jedinjenje **1** kristališe u triklinskom kristalografskom sistemu, prostorna grupa P1, sa parametrima elementarne ćelije a=8,040(2), b=8,160(2), c=13,658(7) Å; α=77,03(3), β=88,95(3), γ=89,22(2) °, V=854,95(8) Å^3, Z=2, D_x=1,229 M gm^{-3}, μ=0,08 mm^{-1}, MoKα zračenje.

Jedinjenje **2** kristališe u ortorombičnom kristalografskom sistemu, prostorna grupa $P2_12_12_1$, sa parametrima elementarne ćelije a=7,225(2), b=8,887(2), c=25,358(8) Å, V=1628,2(2) Å^3, Z=4, D_x=1,270 Mg m^{-3}, μ=0,08 mm^{-1}, MoKα zračenje.

Obe strukture su rešene direktnim metodama primenom SHELXS-97 [1] i utačnjene pomoću SHELXL-97 [1]. Konačni R faktori za jedinjenja **1** and **2** su 0,0486 (za 3683 refleksa sa I>2σ(I)) i 0,0427 (za 1547 refleksa sa I>2σ(I)), respektivno.



molekul **1**



molekul **2**

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

SYNTHESIS AND CRYSTAL STRUCTURE OF (17R)-3,17-DIHYDROXY-16-CYANO-17-METHYL-16,17-SECOESTRA-1,3,5(10)-TRIENE (1) AND 3-BENZYLOXY-17A-METHYL-17-OXA-D-HOMOESTRA-1,3,5-TRIEN-16-ONE (2)

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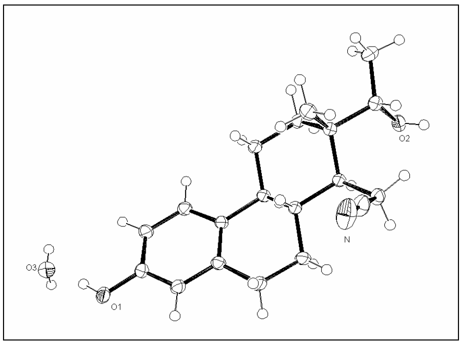
In order to investigate antihormonal activity we were synthesized (17R)-3,17-dihydroxy-16-cyano-17-methyl-16,17-secoestra-1,3,5(10)-triene (**1**) starting from estrone benzyl ether in five synthetic steps. In one of the synthetic steps we were obtained 3-benzyloxy-17a-methyl-17-oxa-D-homoestra-1,3,5-trien-16-one (**2**) as by product.

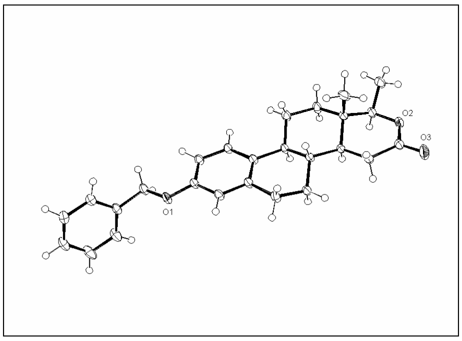
The compound **1** crystallizes in the orthorhombic system, space group $P2_12_12_1$, with the unit cell parameters a=8.218(2), b=9.567(2), c=21.383(7) Å; V=1681.0(8) Å^3, Z=4, D_x=1.183 Mg m^{-3}, μ=0.08 mm^{-1}, MoKα radiation.

The compound **2** crystallizes in the triclinic system, space group P1, with the unit cell parameters a=6.852(2), b=8.744(2), c=9.740(2) Å; α=91.903(3), β=101.881(3), γ=112.525(3)°, V=523.38(8) Å^3, Z=1, D_x=1.239 Mg m^{-3}, μ=0.08 mm^{-1}, MoKα radiation.

Both structures were solved by direct methods using SHELXS-97 [1], and refined by SHELXL-97 [1]. The final R factors for compounds **1** and **2** are 0.0349 (for 5199 reflections with $I>2\sigma(I)$) and 0.0354 (for 6305 reflections with $I>2\sigma(I)$), respectively.



Perspective view of the molecule **1**



Perspective view of the molecule **2**

[1] G. M. Sheldrick, SHELXL-97, *Program for the refinement of crystal structures*, University of Goettingen, Germany (1997).

SINTEZA I KRISTALNA STRUKTURA (17R)-3,17-DIHIDROKSI-16-CIJANO-17-METIL-16,17-SEKOESTRA-1,3,5(10)-TRIENA (1) I 3-BENZILOKSI-17A-METIL-17-OKSA-D-HOMO-ESTRA-1,3,5-TRIEN-16-ONA (2)

O. Klisurić[a], S. Stanković[a], D. Lazar[a], D. Zobel[b], A. Wagner[b], K. Penov-Gaši[a], S. Stajanović[a]

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U cilju ispitivanja antihormonske aktivnosti sintetizovan je (17R)-3,17-dihidroksi-16-cijano-17-metil-16,17-sekoestra-1,3,5(10)-trien (**1**) iz benziletra estrona u pet sintetskih faza. U jednoj od sintetskih faza kao sporedan proizvod reakcije dobijen je 3-benziloksi-17a-metil-17-oksa-D-homoestra-1,3,5-trien-16-on (**2**).

Jedinjenje **(1)** kristališe u ortorombičnom kristalografskom sistemu, prostorna grupa $P2_12_12_1$, sa parametrima elementarne ćelije a=8,218(2), b=9,567(2), c=21,383(7) Å; V=1681,0(8) Å^3, Z=4, D_x=1,183 M gm^{-3}, μ=0,08 mm^{-1}, MoKα zračenje

Jedinjenje **(2)** kristališe u triklinskom kristalografskom sistemu, prostorna grupa P1, sa parametrima elementarne ćelije a=6,852(2), b=8,744(2), c=9,740(2) Å; α=91,903(3), β=101,881(3), γ=112,525(3)°, V=523,38(8) Å^3, Z=1, D_x=1,239 M gm^{-3}, μ=0,08 mm^{-1}, MoKα zračenje.

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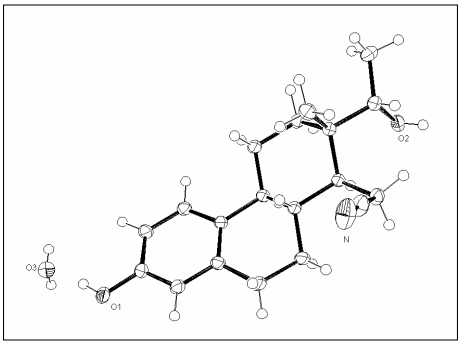
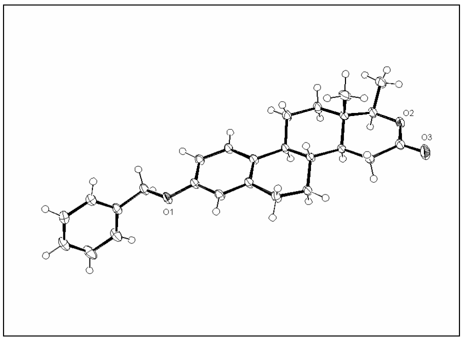


molekul **1**



molekul **2**

[1] G. M. Sheldrick, SHELXL-97, *Program for the refinement of crystal structures*, University of Goettingen, Germany (1997).