

To date, more than 70 acetate uranyl complexes have been researched, while uranyl complexes with anions of other monocarboxylic acids are considerably less studied. Thus, structure of only one uranyl complex with *i*-butyrate ligands is determined [1], and there exists no data about U(VI) compounds containing *n*-butyrate and *n*-valerate ions. In present research we defined crystal structures of $\text{NaUO}_2(\text{n-C}_3\text{H}_7\text{COO})_3 \cdot 0.25\text{H}_2\text{O}$ (I), $\text{KUO}_2(\text{n-C}_3\text{H}_7\text{COO})_3$ (II) and $\text{UO}_2(\text{n-C}_4\text{H}_9\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (III).

I and II were derived as prismatic yellow crystals while studying the interaction between uranyl nitrate and butyric acid in presence of sodium hydroxide (or potassium hydroxide). Prismatic yellow crystals III were derived as a result of interaction between uranium trioxide and aqueous solution of valeric acid. Fundamental absorption bands of UO_2^{2+} , $\text{C}_3\text{H}_7\text{COO}^-$ or $\text{C}_4\text{H}_9\text{COO}^-$ (only for III) ions and water molecules (for I and III) are present in IR spectra of I-III.

Structures of I-III were determined using X-ray diffraction. I crystallizes in the monoclinic system with the unit cell parameters $a = 13.567$, $b = 20.07$, $c = 13.614$ Å, $\beta = 106.839^\circ$, space group $P2_1$, $Z = 8$ and $R = 0.049$. II crystallizes in the orthorhombic system with the unit cell parameters $a = 17.133$, $b = 19.697$, $c = 21.969$ Å, space group $P2_12_12_1$, $Z = 16$ and $R = 0.056$. III crystallizes in the monoclinic system with the unit cell parameters $a = 7.782$, $b = 10.802$, $c = 9.512$ Å, $\beta = 104.885^\circ$, space group $C2/m$, $Z = 2$ and $R = 0.025$. Some butyrate and valerate ions in I-III are disordered over two positions.

Coordination polyhedron of every uranium atom in I-III is hexagonal bipyramid UO_8 with oxygen atoms of uranyl ion located on the main axis. In I and II there are four crystallographic sorts of atoms U and R ($R = \text{Na}$ or K with coordination numbers 6 or 5 (5 – only for Na(3), which is bonded with water molecule in I)). The structural units of I and II are mononuclear groups of the composition $[\text{UO}_2(\text{C}_3\text{H}_7\text{COO})_3]^-$ with crystal chemical formula AB^{01}_3 ($A = \text{UO}_2^{2+}$, $B^{01} = \text{C}_3\text{H}_7\text{COO}^-$) (coordination types of ligands are assigned according to [2]). Tris(butyrate)dioxidouranium(VI) complexes are joined through electrostatic interactions with sodium and potassium cations, and, in I, also through a system of hydrogen bonds with participation of water molecules. The structural units of III are uncharged complexes $[\text{UO}_2(\text{C}_4\text{H}_9\text{COO})_2(\text{H}_2\text{O})_2]$ with crystal chemical formula $AB^{01}_2M^1_2$ ($A = \text{UO}_2^{2+}$, $B^{01} = \text{C}_4\text{H}_9\text{COO}^-$, $M^1 = \text{H}_2\text{O}$), which are joined through a system of hydrogen bonds.

Using TOPOS program package [3], crystal chemical analysis of sodium and potassium uranyl complexes with acetate and butyrate ligands was carried out.

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Keywords: uranyl, butyrate, valerate

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Crystal structure of complexes of uranyl chromate with isomers of pyridinecarboxylic acid

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The structures of uranyl sulfate with some isomers of pyridinecarboxylic acid are described in [1, 2]. To investigate the influence of nature of oxoanions on the structure of the complexes, complexation of uranyl chromate with nicotinic and isonicotinic acid in aqueous solutions was studied and new compound with

compositions $[\text{UO}_2\text{CrO}_4(\text{C}_5\text{H}_4\text{NHCOO})] \cdot \text{H}_2\text{O}$ (I) ($\text{C}_5\text{H}_4\text{NHCOO}$ – piridin-4-carboxylic acid) and $[\text{UO}_2\text{CrO}_4(\text{C}_5\text{H}_4\text{NHCOO})] \cdot 0.25\text{H}_2\text{O}$ (II) ($\text{C}_5\text{H}_4\text{NHCOO}$ – piridin-3-carboxylic acid) were obtained. The structures of I and II were studied by X-ray diffraction. Both compounds crystallize in the monoclinic crystal system. The unit cell parameters for I: $a = 7.5025$, $b = 11.5188$, $c = 13.0518$ Å, $\beta = 97.877^\circ$, $V = 1117.3$ Å³, space group $P2_1/n$, $Z = 4$, $R_f = 0.0263$ (3840 reflections); and for II: $a = 7.2362$, $b = 13.8847$, $c = 10.7204$ Å, $\beta = 90.037^\circ$, $V = 1077.1$ Å³, space group $P2_1/n$, $Z = 4$, $R_f = 0.0236$ (5224 reflections).

The coordination polyhedron of the uranium atom in both structures I and II has the shape of a UO_2O_5 pentagonal bipyramid. In structure I three equatorial oxygen atoms belong to three tridentate chromate ions (T^3 type) and another two oxygen atoms belong to two bidentate bridging molecules of isonicotinic acid (B^2 type), which occupy trans positions in relation to each other in equatorial plane of uranyl ion. The main structural unit of I is a layer $[\text{UO}_2\text{CrO}_4(\text{C}_5\text{H}_4\text{NHCOO})]$ belonging to the AT^3B^2 crystal chemical group, ($A = \text{UO}_2^{2+}$, $T^3 = \text{CrO}_4^{2-}$, $B^2 = \text{C}_5\text{H}_4\text{NHCOO}$ molecules). The designations of coordination types and crystal chemical formulas are given in accordance with [3]. Layers are linked in framework by system of hydrogen bonds, which include outer sphere water molecules. In structure II chromate ions also have tridentate coordination and nicotinic acid molecules are bidentate chelate (B^{01} type). The main structural unit of II is a chain $[\text{UO}_2\text{CrO}_4(\text{C}_5\text{H}_4\text{NHCOO})]$, belonging to the AT^3B^{01} crystal chemical group, ($A = \text{UO}_2^{2+}$, $T^3 = \text{CrO}_4^{2-}$, $B^{01} = \text{C}_5\text{H}_4\text{NHCOO}$ molecules).

Influence of nature of oxoanion and type of isomer on the structure of complexes of uranyl sulfate and chromate with some isomers of pyridinecarboxylic acid was discussed.

This study was supported by the Ministry of Education and Science of the Russian Federation (project no. 02.740.11.0275).

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Keywords: uranyl, structure

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Complexes containing coordination centre OSiC_3X ($\text{X} = \text{Cl}$, Br) based on N-organosulfonyl-2-aminoacids

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Complexes with a coordination centre OSiC_3Cl obtained from N-organosulfonyl-2-aminoacid containing three biologically active moieties (sulphonamide group, the residue of amino acid, and the five-membered O-Si-chelate ring) were studied by x-ray diffraction.

The structural characteristics of the coordination polyhedron of the silicon atom in these complexes and the influence of crystal packing on their molecular structure were analyzed.

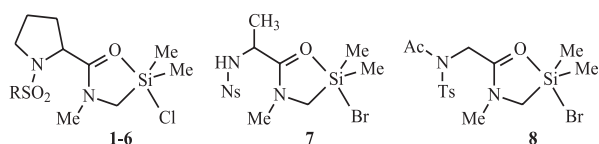
In the case of $\text{X}=\text{Cl}$ the coordination polyhedron of the silicon atom correspond to a distorted trigonal bipyramid. The deviation of the silicon atom from the plane of equatorial substituents varies in the range from $-0.0408(8)$ to $0.0809(3)$ Å (sign “-” means that the Si atom deviates towards the Cl atom). The Si-O bond length depends on the electron-acceptor properties of N-organosulfonylprolin substituent; the smallest value corresponds to the compound **1** ($R = \text{Me}$), and the largest to the compound **2** ($R = \text{Ph}$). The changes in the interatomic Si ... O distances are those for Si ... Cl are antibate ($1.924(2)$ - $2.007(16)$ and $2.256(15)$ - $2.346(11)$ Å, respectively). The strongest intermolecular

interactions in the structures **1-6** are the weak (CH ... O and CH ... Cl) bonds. In addition, in the structure **6** the stacking interactions between the fragments Ph-NO₂ are observed.

The derivatives of glycine and alanine (**7** and **8**) can be described as “freeze” cation-anion pairs. The Si...Br interatomic distances (2.7095(8) and 2.9704(7) Å, for **7** and **8**, respectively) are much larger than those in the compounds of tetracoordinated Si (for instance, in the tris(pentafluorophenylmethyl)silylbromide the corresponding bond length is 2.208 Å). In turn, the Si-O bond in **7** and **8** is considerably shorter than in **1-6**. In contrast to **1-6**, the coordination polyhedron corresponds to the distorted tetrahedron with weak additional Si-O coordination bond.

To estimate the energy of intermolecular interactions, we have carried out quantum chemical calculations of the isolated molecules **7-8** and their associates. Also, the solid-state MAS ²⁹Si spectra of **7** and **8** were simulated using plane-wave DFT calculations.

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1: R=Me, 2: R=Ph, 3: R=p-MeC₆H₄, 4: R=p-ClC₆H₄, 5: R=p-BrC₆H₄, 6: R=p-NO₂C₆H₄

Keywords: N-organosulfonyl-2-aminoacids, hypervalent silicon, crystal packing

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The influence of crystal packing on the structure of N-organosulfonyl-2-aminoacid complexes containing OSiC₃F coordination unit

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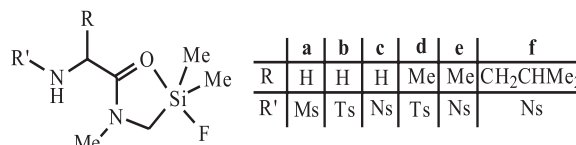
Silylfluorides with pentacoordinated Si atom obtained from N-organosulfonyl-2-aminoacids contain bioactive fragments and have high hydrolytic stability. In this study, we analyzed the influence of crystal packing on the geometry of coordination environment of the silicon atom in six pentacoordinated silylfluorides containing OSiC₃F coordination polyhedron.

Taking into account similar inductive effect of exocyclic substituents in the complexes **a-f**, one would expect the coordination site of the silicon atom to have a similar structure. Indeed, in all cases OSiC₃F coordination polyhedron corresponds to a distorted trigonal pyramid. The deviation of the silicon atom from the plane of the equatorial C atoms varies within a fairly narrow range of 0.05 Å. The Si-O bond length decreases along with an increase in Si-F one. These bonds vary in the ranges of 2.135(2)-2.384(1) and 1.681(2)-1.646(1) Å, respectively. Observed differences in the lengths of the Si-O bond are mainly related to intermolecular interactions rather than to the nature of R and R' substituents. The presence of strong N-H...F bonds causes a strengthening of the coordination bond Si-O. In contrast, the formation of a N-H...O bond with the endocyclic O atom leads to weakening of the Si-O coordination bond.

In the solid state, molecules **a** and **e** form chains via N-H...F and N-H...O bonds, respectively; in the cases of **c**, **d** and **f** complexes, centrosymmetric dimers are formed via N-H...O bonds with carbonyl (**d** and **f**) and sulfonyl (**c**) groups of neighboring molecules. The

shortest Si-O bond is observed in the structure of **e**, where F atom is involved in N-H...F hydrogen bond, which leads to the weakening of Si-F bond. In turn, the longest Si-O bond is found in the structure of **b** (2.384(1) Å), which is the maximum value for all the earlier described complexes with OSiC₃F coordination polyhedron; the reason for this being is the intramolecular N-H...O hydrogen bond. Quantum chemical calculations of isolated molecules and their dimers were carried out to evaluate the energy of hydrogen bonds.

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Keywords: N-organosulfonyl-2-aminoacids, hypervalent silicon, crystal packing

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Crystal structure of [Cu₂(L)₂(H₂O)₂](SO₄)₂·2H₂O (L = pyridoxal thiosemicarbazone)

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Dark red monocystals of the title complex were prepared by the reaction of methanol solutions of CuSO₄·5H₂O and pyridoxal thiosemicarbazone (L) in mole ratio 1:1. Dinuclear complex cation has centrosymmetric structure. The Cu(II) is situated in a square-pyramidal environment ($\tau = 0.039$). The equatorial plane is formed by chelate ONS coordination of L and one water molecule, while the apical position is occupied by an alcoholic oxygen O(2)ⁱ ($i = -x, 1-y, -z$) of the bridging ligand. The same way of coordination was reported for a similar ligand [1]. The Cu atom is shifted towards the apical oxygen atom by 0.173(12) Å. The Cu-atom ligand bond lengths are in the range 1.917(2)-1.967(2) Å for O(1) N(3) and O(7), while Cu-S(1) and Cu-O(2)ⁱ are longer (2.2998(9) Å and 2.233(2) Å, respectively). Pyridoxal thiosemicarbazone is coordinated in neutral, zwitterionic form as tetradentate bridging ligand, *i.e.* via phenol oxygen, hydrazine nitrogen, thioamide sulfur and hydroxymethyl oxygen, which, as the bridging ligand, connects the subunits. Such coordination results in formation of two metalocycles, five-membered (thiosemicarbazide) and six-membered (pyridoxilidene). The coordinated ligand slightly deviates from planarity, and dihedral angles between pyridine ring, six- and five-membered metalocycles are 7.54(10)°, 4.80(7)°, respectively. The six-membered metalocycle is in screw-boat conformation and can be described by the following puckering parameters: $Q = 0.200(2)$ Å, $\theta = 67.9(9)^\circ$, $\phi = 34.3(9)^\circ$, while the other rings are planar. Crystal structure of the complex is stabilized by an extended inter- and intramolecular 3D hydrogen-bond network. It can be mentioned that all possible hydrogen donors are involved in hydrogen-bonding, and that sulfate anion acts as multiple hydrogen acceptor.

The data were collected on an Oxford Diffraction Gemini S diffractometer using MoK α radiation ($\lambda = 0.71069$ Å), and were corrected for Lorentz, polarization and background effects. The structure was solved by direct methods using SIR92 and refined by full matrix least square methods on F^2 using SHELXL-97 to $R = 0.036$. Crystallographic data: C₁₈H₃₂Cu₂N₈O₁₆S₄, Mr = 871.90, monoclinic, space group $P2_1/n$, $a = 7.2529(2)$ Å, $b = 11.1766(4)$ Å, $c = 18.8522(6)$ Å, $\beta = 93.751(3)^\circ$, $V = 1524.94(8)$ Å³, $Z = 2$, $\mu(\text{MoK}\alpha) = 1.756$ mm⁻¹, GooF = 1.059.