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Synthesis and Structure of a New Uranyl Selenate Complex with 1-Butylamine $[CH_3(CH_2)_3NH_3](H_5O_2)[(UO_2)_2(SeO_4)_3(H_2O)]$

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Abstract—Crystals of a new uranyl selenate complex $[CH_3(CH_2)_3NH_3](H_5O_2)[(UO_2)_2(SeO_4)_3(H_2O)]$ were obtained by isothermal evaporation at room temperature of its aqueous solution. The crystal structure was determined by the X-ray diffraction analysis. The observed character of the arrangement of organic molecules in the interlayer space confirms the concept of hydrophilic and hydrophobic zones.

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Recently the structural chemistry of inorganic compounds of actinides has been enriched by the discovery of nano-sized clusters [1, 2] based on the oxides of uranium, neptunium, and plutonium, as well as uranyl selenate nanotubulenes [3–5], which are considered as the first examples of actinide-containing nanostructures [6, 7]. With a number of examples of organic-inorganic compounds with uranyl selenate complexes and amines of various composition and structure the role has been demonstrated of hydrophilic-hydrophobic interactions in self-assembly of supramolecular organic units and their impact on the topology and geometry (in particular, curvature) of inorganic complex [8–13]. In particular, in [8, 9] we have proposed the concept of hydrophilic-hydrophobic zones, according to which the uranyl topology in the different amine-templated uranyl compounds with the same composition of the inorganic complex is controlled by the ratio and packing of hydrophilic and hydrophobic parts of the protonated amine molecules. In this paper we demonstrate the effectiveness of this concept by the example of the crystal structure of uranyl selenate complex $[CH_3(CH_2)_3NH_3](H_5O_2)[(UO_2)_2\cdot(SeO_4)_3(H_2O)]$ (**I**) where the structure of the inorganic uranyl selenate complex is determined by the structural features of interlayer packing of protonated molecules of 1-butylamine and water molecules.

The X-ray diffraction analysis was carried out on a Stoe IPDS II diffractometer equipped with X-ray sensitive plate with optical memory (Image Plate). The unit cell parameters (Table 1) were defined and refined by least-squares method based on 9971 reflections ($2\theta = 3.80°–58.44°$). Extinguishing laws and statistics of the reflections distribution correspond to space group $P2_1$. The extinction correction was introduced with accounting for the crystal shape. The structure was solved by direct methods and refined to $R_1 = 0.0454$ ($wR_2 = 0.1103$) for 4861 reflections with $|F_0| \geq 4\sigma_F$ using the program SHELXL-97 [14]. Positions of hydrogen atoms were calculated with the algorithms of the SHELXL software. The final model included the coordinates and anisotropic thermal parameters for all nonhydrogen atoms. Table 2 lists the obtained interatomc distances. Supplementary crystallographic data on the structure of compound **I** are deposited in the Cambridge Crystallographic Database (CCDC 800423).

The structure of **I** is based on the layered complexes of composition $[(UO_2)_2(SeO_4)_3(H_2O)]^{2-}$ (Fig. 1), parallel to (100) plane, that consist of the coordination polyhedra of uranium and selenium, combined via bridging oxygen atoms. A cell of structure **I** contains two crystallographically nonequivalent uranium atoms, each forms $U^{6+}–O^{2-}$ bonds: two short (1.750–1.768 Å) forming the uranyl cation $[UO_2]^{2+}$, and five longer (2.340–2.486 Å) in the equatorial plane of uranyl, which leads to the formation of pentagonal–bipyramidal coordination around

Table 1. Crystallographic data and refinement parameters of the structure **I**[a]

Parameter	Value
a, Å	8.3908(11)
b, Å	12.3602(11)
c, Å	10.9150(13)
α, deg	90.00
β, deg	101.567(10)
γ, deg	90.00
V, Å^3	1109.0(2)
Space group	$P2_1$
μ (mm^{-1})	19.588
Z	2
d_{calc}, g cm^{-3}	3.267
Crystal size (mm^3)	0.16×0.10×0.08
Radiation	MoK_α
Total reflections	9971
Independent reflections	5405
Measuring range 2θ, deg	3.80–58.44
Reflections with $\lvert F_0\rvert \geq 4\sigma_F$	4861
R_{int}	0.0744
R_σ	0.0713
R_1 ($\lvert F_0\rvert \geq 4\sigma_F$)	0.0456
wR_2 ($\lvert F_0\rvert \geq 4\sigma_F$)	0.1095
R_1 (all data)	0.0531
wR_2 (all data)	0.1128
S	1.070
$\rho_{\min}$, $\rho_{\max}$, e Å^{-3}	–3.545, 1.277

[a] $R_1 = \Sigma\lvert\lvert F_0\rvert - \lvert F_\mathrm{c}\rvert\rvert/\Sigma\lvert F_0\rvert$; $wR_2 = \{\Sigma[w(F_0^2 - F_\mathrm{c}^2)2]/\Sigma[w(F_0^2)2]\}^{1/2}$; $w = 1/[\sigma^2(F_0^2)+(aP)^2 + bP]$, где $P = (F_0^2 + + 2F_\mathrm{c}^2)/3$; $s = \{\Sigma[w(F_0^2 - F_\mathrm{c}^2)]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

Table 2. Selected interatomic distances (*d*, Å) and angles (ω, deg) in the structure **I**

Bond length		Bond length	
U^1O^{11}	1.763(12)	Se^2O^{12}	1.598(14)
U^1O^7	1.767(12)	Se^2O^{13}	1.619(10)
U^1O^6	2.341(11)	Se^2O^{14}	1.652(12)
U^1O^{10}	2.354(11)	Se^2O^2	1.656(10)
U^1O^2	2.358(11)	$\langle Se^2O\rangle$	1.631
U^1O^3	2.432(10)		
U^1O^4	2.484(11)	Se^3O^{16}	1.607(13)
$\langle U^1O_{Ur}\rangle$	1.765	Se^3O^{15}	1.623(12)
$\langle U^1O_{eq}\rangle$	2.394	Se^3O^3	1.643(10)
		Se^3O^6	1.650(10)
U^2O^9	1.750(12)	$\langle Se^3O\rangle$	1.631
U^2O^8	1.757(11)		
U^2O^{15}	2.350(11)	N^1C^2	1.481(18)
U^2O^{14}	2.367(10)	C^1C^3	1.410(19)
U^2O^{13}	2.385(11)	C^1C^4	1.437(19)
U^2O^5	2.427(10)	C^2C^3	1.412(19)
U^2O^1	2.435(12)	Angle	
$\langle U^2O_{Ur}\rangle$	1.754	$Se^1O^1U^2$	140.4(8)
$\langle U^2O_{eq}\rangle$	2.393	$Se^1O^5U^2$	138.2(7)
		$Se^1O^{10}U^1$	147.0(7)
Se^1O^{17}	1.634(14)	$Se^2O^2U^1$	137.1(7)
Se^1O^1	1.640(11)	$Se^2O^{13}U^2$	137.5(7)
Se^1O^5	1.643(11)	$Se^2O^{14}U^2$	133.3(7)
Se^1O^{10}	1.653(11)	$Se^3O^3U^1$	132.5(5)
$\langle Se^1O\rangle$	1.642	$Se^3O^6U^1$	135.8(6)
		$Se^3O^{15}U^2$	143.3(7)

the uranium. In structure **I** there are two types of the uranyl coordination polyhedra: pentagonal bipyramids U^2O_7 and bipyramids $U^1O_6(H_2O)$. The tetrahedrally coordinated selenate tetrahedra SeO_4 are tridentate-bridging. The selenate tetrahedra lie in the plane of the inorganic layer forming the bonds with the uranium polyhedra at the three vertexes, while the fourth vertex of each tetrahedron is oriented upward or downward relative to the layer plane.

The graph theory analysis [14, 15] of the topology of the uranyl selenate layer (Fig. 2) in the structure **I** showed that the topology at the combining the coordination polyhedra in the complex belongs to the type 12/3j, which is quite widespread among the uranyl selenates [1]. The 12/3j graph comprises four- and six-membered rings. The six-membered rings are connected through common vertices into chains extended along the [010] direction.

The charge of the inorganic layer $[(UO_2)_2(SeO_4)_3\cdot(H_2O)]^{2-}$ is compensated by protonated molecules of 1-butylamine and the complexes $(H_5O_2)^+$ located in the interlayer space.

As shown in [8, 9], in the structures with uranyl selenate layers $[(UO_2)_2(SeO_4)_3(H_2O)]^{2-}$ the layer

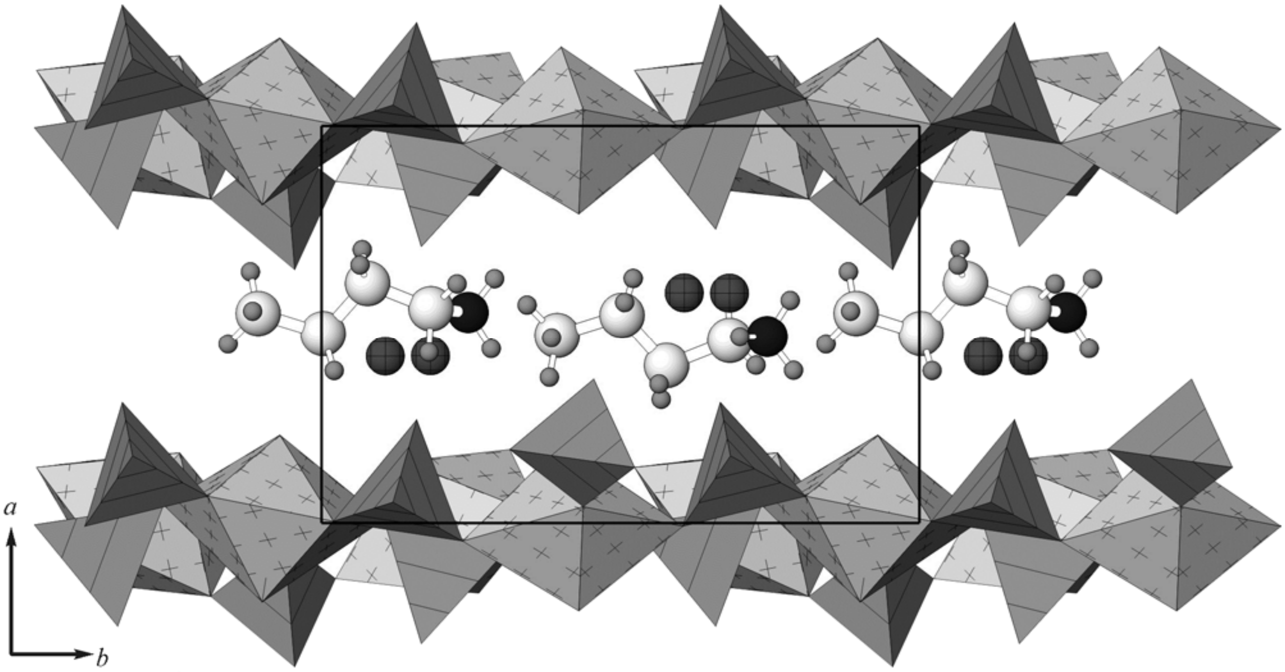

Fig. 1. The crystal structure of compound **I** projected on (001) plane. Uranyl bipyramids and selenate tetrahedra are shown as light-gray and gray structures, respectively. The N and C aatoms are shown as black and white circles, respectively. The O atoms of oxonium complexes are shown as dark-gray circles.

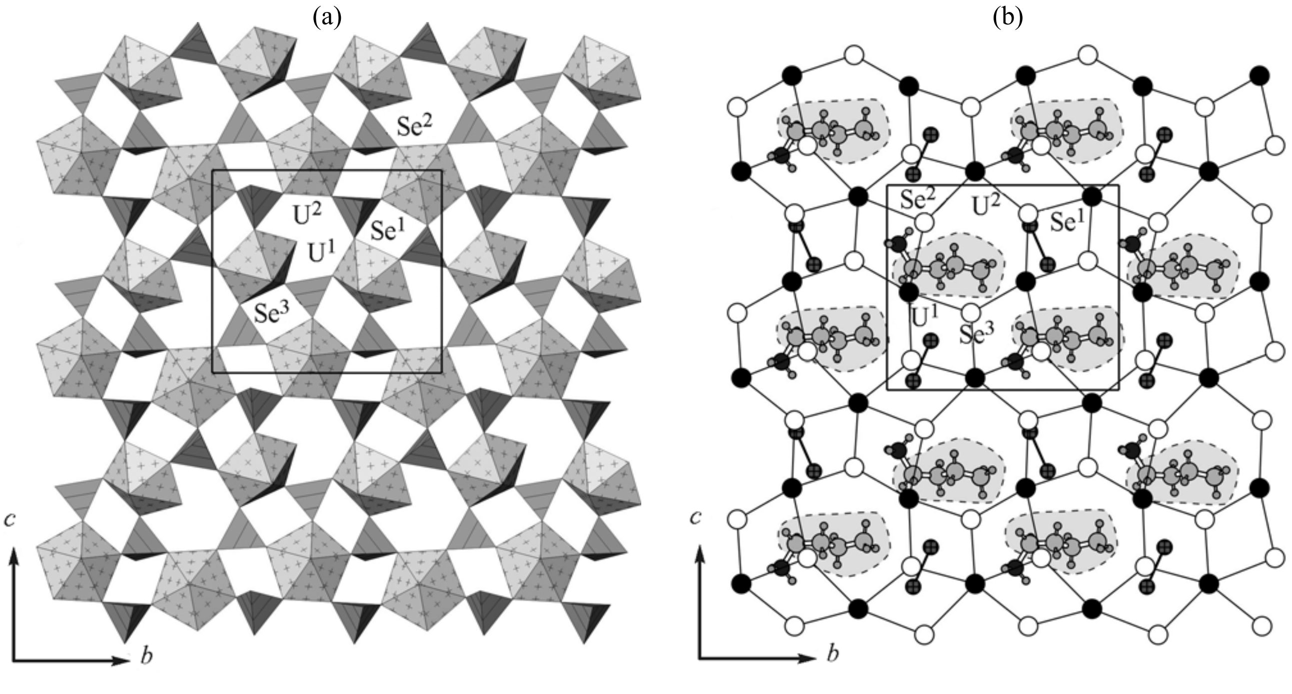

Fig. 2. Uranyl selenate layer structure in the compound **I** (a) and the graph of this layer (b) (black and white nodes represent the coordination polyhedra of uranium and selenium, respectively) overlaid with the protonated 1-butylamine molecules (the dashed line indicates the hydrocarbon chain of the molecules) and the oxonium complexes O atoms (shown as dark-gray circles).

topology at the formation of the structure is controlled by the structural features and packing of the protonated amine molecules. Consider the packing of the butylamine protonated molecules, $CH_3(CH_2)_3NH_3^+$, and water complexes $H_5O_2^+$ in the interlayer space of structure **I** (Fig. 2). Hydrocarbon fragments of the organic molecules form a hydrophobic zone arranged along the *b* axis, while the hydrophilic $–NH_3$ ends are associated with the oxonium molecules and form the zones elongated in the same direction. When comparing the graph of the inorganic layer and the packing of organic molecules, it becomes apparent that the chain of six-membered rings in the inorganic layer is also arranged along the *b* axis, and their location corresponds to the location of hydrophobic zones. At the same time, the hydrophilic zones of interlayer packing are associated with the set of the dense four-membered ring.

Thus, the results of solving the crystal structure of compound **I** confirm the concept of hydrophilic and hydrophobic areas that we have proposed in [8, 9] which describes the character of the organic substructure as defining the topology of inorganic uranyl selenate complexes. In structure **I** the hydrocarbon parts of organic molecules are associated with large six-membered ring, whereas the amine ends of the molecules tend to approach the dense four-membered rings.

EXPERIMENTAL

Single crystals of compound **I** were prepared by evaporation of aqueous solution containing uranyl nitrate, selenic acid, and 1-butylamine, the ratio $UO_2(NO_3)_2 \cdot 6H_2O:CH_3(CH_2)_3NH_2$ = 1:2, 0.05 g of $UO_2(NO_3)_2 \cdot 6H_2O$, 0.1 ml of $CH_3(CH_2)_3NH_2$, 0.2 ml of H_2SeO_4, 2 ml of H_2O. The transparent plate crystals of yellow-green color suitable for X-ray diffraction study formed at the bottom of watch glass on the third day of the experiment.

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