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Crown-ether-templated uranyl selenates: novel family of mixed organic-inorganic actinide compounds

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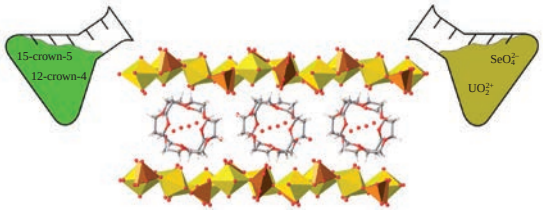
Two novel uranyl-selenate oxysalts templated by the electro-neutral 12-crown-4 and 15-crown-5 molecules are obtained from aqueous solutions under ambient conditions. The arrangement of organic molecules between the uranyl-selenate layers is provided only by means of protonated water molecule complexes.



Within the last decade explorative studies of uranium-containing systems revealed an amazing variety of structural architectures of the natural and synthetic hexavalent uranium compounds. The structural diversity is largely derived from the wide range of chemical compositions: uranyl ions linked *via* bridged oxygen atoms to another high-valent cations (Cr^{6+}, Mo^{6+}, P^{3+}, P^{5+}, S^{6+}, Se^{4+}, Se^{6+}, *etc*.) with organic and inorganic cations of different shapes and valence states separating uranyl-containing heteropolyhedral units from each other.[1–4] There are very few reported uranium compounds with crown-ether molecules and almost all of them possess some unique and remarkable structures: nanotubular or microporous,[5] rare 0-D and 1-D units,[6,7] and structures with symmetrical hydrogen bonds between selenate tetrahedra.[8] The arrangements of crown-ether molecules between the uranyl-based structural units involve several types of bonding: strong ionic forces, hydrogen bonding and van der Waals interactions. As a continuation of this topic, several experiments in the aqueous systems containing U^{VI}, Se^{VI} and crown-ether molecules yielded three novel uranyl-selenate oxysalts, namely† $[(H_5O_2)_3(H_9O_4)](C_8H_{16}O_4)_2[(UO_2)_2(SeO_4)_3(H_2O)]_2$ **1**, $[(H_5O_2)(H_3O)_3](C_{10}H_{20}O_5)[(UO_2)_3(SeO_4)_5(H_2O)]$ **2** and $[(H_5O_2)_x(H_3O)_{4-x}](C_{10}H_{20}O_5)[(UO_2)_3(SeO_4)_5(H_2O)](H_2O)_y$ **3** with interactions between organic and inorganic substructures provided through the protonated H_2O molecular units.‡

Crystal structure of compound **1** contains two symmetrically non-equivalent U^{6+} atoms with two short U^{6+}=O^{2-} bonds [1.740(11) and 1.755 (11) Å for U(1); 1.745(11) and 1.748(10) Å for U(2)] forming approximately linear UO_2^{2+} uranyl cations

† Crystals of compounds **1**–**3** were prepared by isothermal evaporation from aqueous solutions at room temperature. The crystals of compound **1** were synthesized by the reaction of 0.051 g (0.1 mmol) of $UO_2(NO_3)_2 \cdot 6H_2O$, 0.040 g (0.22 mmol) of 12-crown-4, 0.280 g (2.0 mmol) of 40% H_2SeO_4, and 2.001 g (111.2 mmol) of deionized distilled water. Compound **2**: 0.050 g (0.1 mmol) of uranyl nitrate, 0.046 g (0.21 mmol) of 15-crown-5, 0.282 g (2.0 mmol) of selenic acid, and 2.012 g (111.7 mmol) of deionized distilled water. Compound **3**: 0.050 g (0.1 mmol) of uranyl nitrate, 0.046 g (0.21 mmol) of 15-crown-5, 0.282 g (2.0 mmol) of selenic acid, and 2.012 g (111.7 mmol) of deionized distilled water (note: the bulk of crystals here belongs to compound **2**). Homogeneous liquid solutions were left in a watch glass. Yellowish-green flattened crystals formed within 2 weeks.

‡ *Crystallographic data*. The crystals of compounds **1**–**3** are monoclinic.

For **1**: $C_{16}H_{36}O_{52}Se_6U_4$, M = 2486.33, $P2_1/c$, a = 10.7328(6), b = = 12.2828(5), and c = 22.7085(17) Å, β = 110.102(5)°, V = 2811.3(3) Å^3, Z = 2.

For **2**: $C_{10}H_{22}O_{37}Se_5U_3$, M = 1843.16, $P2_1/m$, a = 11.6754(5), b = = 18.9887(10), and c = 12.2047(5) Å, β = 112.282(3)°, V = 2503.7(2) Å^3, Z = 2.

For **3**: $C_{10}H_{22}O_{38}Se_5U_3$, M = 1859.16, $C2/c$, a = 24.2575(15), b = = 11.7501(7), and c = 18.9243(12) Å, β = 101.996(1)°, V = 5276.2(6) Å^3, Z = 4.

All crystals were mounted on thin glass fibers for X-ray diffraction analysis, which was carried out using a STOE single-crystal X-ray diffractometer equipped with IPDS II area detector (compounds **1** and **2**) or a Bruker SMART single-crystal X-ray diffractometer equipped with APEX II CCD area detector (compound **3**) operated with MoKα radiation at 50 kV and 40 mA at room temperature. A hemisphere of X-ray diffraction data (θ_{max} = 25.50 and 27.50° for **1** and **2**, respectively) with frame widths of 2.0° in ω, and exposion of 2 min spent per each frame were collected. More than a hemisphere of X-ray diffraction data (θ_{max} = 27.50°) with frame widths of 0.5° in ω, and exposion of 60 s spent per each frame were collected for compound **3**. Diffraction data were integrated and corrected for background, Lorentz, and polarization effects using the STOE programs X-AREA and X-RED (compounds **1** and **2**) or an empirical spherical model by means of the Bruker programs APEX2 and XPREP (compound **3**). The absorption correction was introduced by numerical integration taking into account the experimentally determined and optimized crystal shape by X-SHAPE algorithm using X-RED program[16] (compounds **1** and **2**) or the SADABS program[17] (compound **3**). The unit cell parameters of compound **1** were determined and refined by the least-squares techniques on the basis of 17 608 reflections with 2θ in the range of 3.82–51.00°. The structure was solved by direct methods and refined to R_1 = 0.057 (wR_2 = 0.111) for 4026 reflections with $|F_0| \geqslant 4\sigma F$. The unit cell parameters of compound **2** were determined and refined by the least-squares techniques on the basis of 20 560 reflections with 2θ in

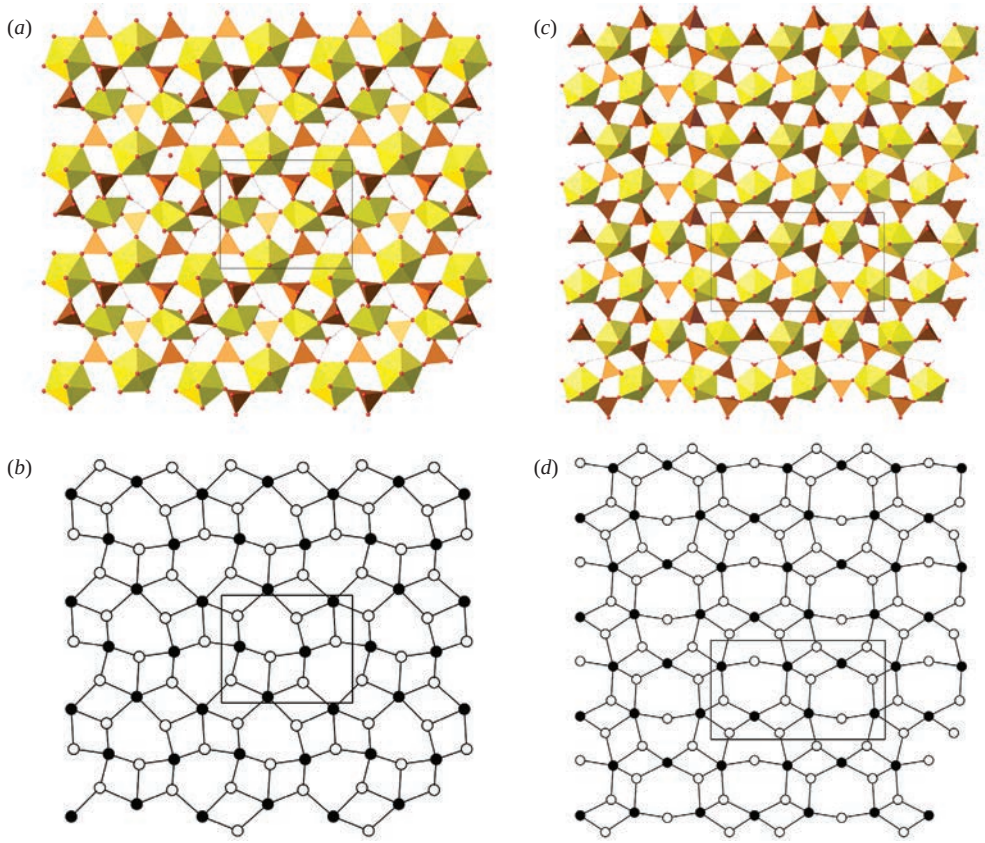


Figure 1 Uranyl selenate 2-D units in compounds (*a*) **1** and (*c*) **2** shown in polyhedra and graphical representation of the layer topology in (*b*) **1** and (*d*) **2**. Uranyl selenate layers in compounds **2** and **3** are topologically equivalent. Legend: U polyhedra are light, Se tetrahedra are dark, (●) U atoms, (○) Se atoms.

(Ur). The $U(1)O_2^{2+}$ cation is coordinated by five oxygen atoms [U(1)–O_{eq}, 2.363(8)–2.432(9) Å] that belong to the selenate oxyanions. The $U(2)O_2^{2+}$ cation is coordinated by four oxygen atoms [U(2)–O_{eq}, 2.365(9)–2.415(10) Å] that belong to the selenate oxyanions and one oxygen atom of an H_2O molecule [U(2)–H_2O(7), 2.494(10) Å] arranged in the equatorial plane of the $Ur(2)O_5$ pentagonal bipyramid. Three symmetrically non-equivalent Se^{6+} atoms are tetrahedrally coordinated by four O^{2-} atoms each [Se–O, 1.629, 1.622 and 1.617 Å for Se(1), Se(2) and Se(3), respectively]. The U and Se coordination polyhedra polymerize by sharing common O atoms to form two-dimensional uranyl selenate $[(UO_2)_2(SeO_4)_3(H_2O)]^{2-}$ anionic layers [Figure 1(*a*)]. Their topology corresponds to the black-and-white graph shown in Figure 1(*b*). This topology is one of the most representative among the 2-D uranyl complexes,[9] but has been observed only in organically templated uranyl compounds (see, *e.g.*, $(C_4H_{12}N)(H_5O_2)[(UO_2)_2(SeO_4)_3(H_2O)]$[10] and $[C_6H_{18}N_2][(UO_2)_2(SeO_4)_3(H_2O)]$[11]). In addition, this type of topology has been identified for the layered structure of inorganic neptunyl chromate $K_2[(NpO_2)_2(CrO_4)_3(H_2O)](H_2O)_3$.[12] The $[SeO_4]^{2-}$ tetrahedra in the structure of **1** are tridentate, sharing three vertices with the adjacent uranium polyhedra, while the fourth vertex is arranged up- or downward with respect to the uranyl selenate sheet.

Crystal structure of compound **2** contains two symmetrically non-equivalent U^{6+} atoms with two short U=O_{Ur} bonds [1.724 and 1.746 Å for U(1) and U(2), respectively] forming Ur. The $U(1)O_2^{2+}$ cation is coordinated by four oxygen atoms [U(1)–O_{eq}, 2.360(8)–2.362(9) Å] that belong to the selenate oxyanions and one oxygen atom of the H_2O molecule [U(1)–H_2O(11), 2.535(12) Å] arranged in the equatorial plane of the $Ur(1)O_5$ pentagonal bipyramid. The $U(2)O_2^{2+}$ cation is coordinated by five oxygen atoms [U(2)–O_{eq}, 2.329(9)–2.448(8) Å] that belong to the selenate oxyanions only. Three symmetrically non-equivalent Se^{6+} atoms are tetrahedrally coordinated by four O^{2-} atoms [Se–O bond length is 1.626, 1.617 and 1.624 Å for Se(1), Se(2) and Se(3), respectively]. Note that the U(1) and Se(3) atoms occupy the special position on the mirror plane in the structure of compound **2**. The arrangement of the U^{6+} and Se^{6+} coordination polyhedra results in the formation of $[(UO_2)_3(SeO_4)_5(H_2O)]^{4-}$ layered complexes [Figure 1(*c*)] with topological type that is not so widespread as that in compound **1**. However, this topological type has been found in six other uranyl selenates [Figure 1(*d*)]:[9] one of them is pure inorganic compound $Rb_4[(UO_2)_3(SeO_4)_5(H_2O)]$,[13] and other five are organically templated uranyl selenates (see, *e.g.* $[C_2H_8N]_3[H_3O][(UO_2)_3(SeO_4)_4(SeO_3)(H_2O)](H_2O)$[14]). Note that all known compounds with this topological type, except for Rb compound, have protonated complexes (H_2O or SeO_4 polyhedra) in their structure indicating very high acidity needed for the formation of their crystals.

Crystals of compound **3** belong to the phase with the topologically similar uranyl selenate $[(UO_2)_3(SeO_4)_5(H_2O)]^{4-}$ layers

the range of 3.77–55.00°. The structure was solved by direct methods and refined to $R_1 = 0.059$ ($wR_2 = 0.148$) for 4385 reflections with $|F_0| \geqslant 4\sigma F$. The unit cell parameters of **3** were determined and refined by the least-squares techniques on the basis of 28 594 reflections with 2θ in the range of 3.43–55.00°. The structure was solved by direct methods and refined to $R_1 = 0.040$ ($wR_2 = 0.108$) for 4199 reflections with $|F_0| \geqslant 4\sigma F$. Crystal structures of compounds **1**–**3** were solved and refined using the SHELX program[18] incorporated in the OLEX2 program package.[19] The final models included coordinates and anisotropic displacement parameters for all non-hydrogen atoms. The carbon-bound H atoms were placed in calculated positions and were included in the refinement in the 'riding' model approximation, with U_{iso}(H) set to 1.2U_{eq}(C) and C–H 0.97 Å. Positions of H atoms of U coordinating water molecules were localized from difference Fourier maps and kept fixed during refinement. Positions of H atoms of hydronium cations were not localized.

CCDC 1421819–1421821 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

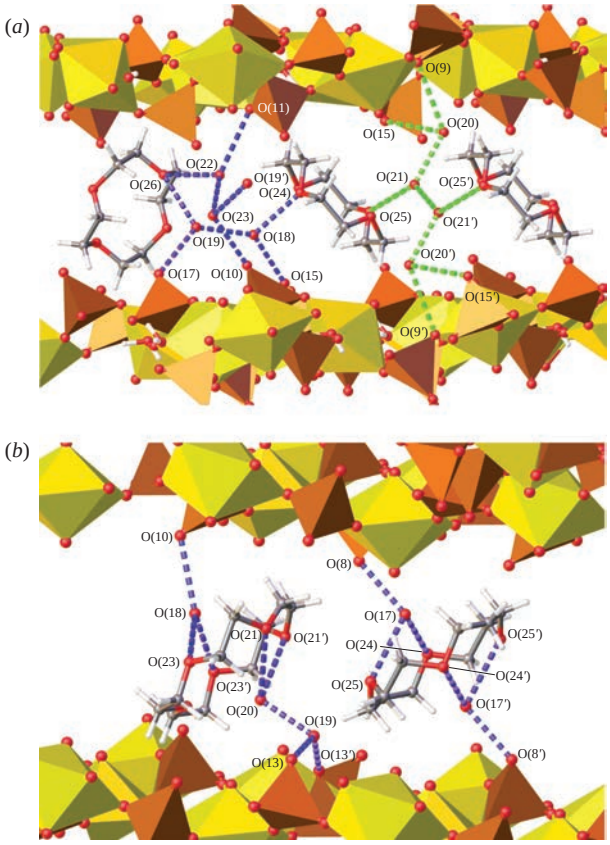


Figure 2 Arrangement of the protonated water molecules in the interlayer space of the structures (*a*) **1** and (*b*) **2**. Hydrogen bonding network of the hydronium and the Zundel cations is shown with dark dashed lines, bonding of $H_9O_4^+$ complex is shown with light dashed lines.

as in compound **2**. However, considerable disorder is observed in the interlayer space, especially related to the water complexes (residual density peaks are 1.5–2.8 e$Å^{-3}$). We were unable to attribute the exact positions of oxygen atoms to the charge-balancing ions, but the refinement of the 2-D unit looks reasonable. There are three crystallographically nonequivalent positions of oxygen atoms in the interlayer space of the structure of compound **3**. Taking into account the multiplicity of their common positions and interatomic distances these O atoms can be attributed to the formula $[(H_5O_2)_2(H_3O)_2]^{4+}$. However, the relatively high displacement parameters, especially for those forming $(H_5O_2)^+$ cation, may indicate a partial occupancy or disordering at the position of molecule. In case of partial occupancy, this complex should be considered as $(H_3O)^+$, whereas the disordering should be regarded as the consequence of displacement of molecule due to the hydrogen bonding with different O atoms of crown ether. The arrangement of the residual electron density peaks near the existing atoms or at a distance of more than 3 Å from them does not yield the assignment of other possible protonated water complexes. However, these peaks could be regarded as partially occupied positions of the water molecules. Unfortunately, the quality of the diffraction data does not allow one to reach more accurate description of the hydronium complexes, but apparently it should be the choice between $(H_5O_2)^+$ and $(H_3O)^+$. Therefore, the data for compound **3** are not discussed here in detail but reported as a structural model with suggested formula as $[(H_5O_2)_x(H_3O)_{4-x}](C_{10}H_{20}O_5)[(UO_2)_3(SeO_4)_5(H_2O)](H_2O)_y$.

The 12-crown-4 (in compound **1**) and 15-crown-5 (in compound **2**) molecules fill interlayer space in such a way that the mean planes of rings are not parallel to the planes of the uranyl selenate layers, but tilted by 33.8 and 73.0° in compound **1** and by 44.7 and 51.6° in compound **2**.

The negative charge of the 2-D uranyl selenate units in the structures of compounds **1** and **2** is compensated by the protonated H_2O complexes arranged between the inorganic sheets. Three types of protonated molecules have been found in the reported compounds: rather usual hydronium cation $(H_3O)^+$, the Zundel cation $(H_5O_2)^+$, and less common linear $(H_9O_4)^+$ cation.[15] Protonated water molecules form branched hydrogen bonding networks (Figure 2) that act as a thread, linking neighboring uranyl selenate layers with beaded rings of crown ethers.

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