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Topologically and geometrically flexible structural units in seven new organically templated uranyl selenates and selenite–selenates

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ABSTRACT

Single crystals of seven novel uranyl oxysalts of selenium with protonated methylamine molecules, $[C_2H_8N]_2[(UO_2)(SeO_4)_2(H_2O)]$ (**I**), $[C_2H_8N]_2[(UO_2)_2(SeO_4)_3(H_2O)]$ (**II**), $[C_4H_{15}N_3][H_3O]_{0.5}[(UO_2)_2(SeO_4)_{2.93}(SeO_3)_{0.07}(H_2O)](NO_3)_{0.5}$ (**III**), $[C_2H_8N]_3[H_5O_2][(UO_2)_2(SeO_4)_3(H_2O)_2]_2(H_2O)_5$ (**IV**), $[C_2H_8N]_2[H_3O][(UO_2)_3(SeO_4)_4(HSeO_3)(H_2O)](H_2SeO_3)_{0.2}$ (**V**), $[C_4H_{12}N]_3[H_3O][(UO_2)_3(SeO_4)_5(H_2O)]$ (**VI**), and $[C_2H_8N]_3(C_2H_7N)[(UO_2)_3(SeO_4)_4(HSeO_3)(H_2O)]$ (**VII**) have been prepared by isothermal evaporation from aqueous solutions. Their crystal structures have been solved by direct methods and their uranyl selenate and selenite–selenate units investigated using black-and-white graphs from the viewpoints of topology of interpolyhedral linkages and isomeric variations. The crystal structure of **IV** is based upon complex layers with unique topology, which has not been observed previously in uranyl selenates. Investigations of the statistics and local distribution of the $U–O_{br}–Se$ bond angles demonstrates that shorter angles associate with undulations, whereas larger angles correspond to planar areas of the uranyl selenite layers.

1. Introduction

Within the last decade actinide oxysalts attracted significant attention due to their importance in mineralogy, uranium mining technologies and studies related to the advanced nuclear fuel cycle. The diversity of polyhedral units found in uranyl compounds is unique, starting from isolated complexes [1–3] and clusters [4–7] to cage compounds [8–11] and nanotubules [12–14]. Selenium-containing uranyl oxysalts are known for both mono- and divalent inorganic cations [15–19], as well as for organic template molecules of various charge and structure [20–24]. The crystal structures of uranyl selenates and selenites are based upon a variety of complex units formed by polymerization of U and Se coordination polyhedra. The topology and geometry of these units is controlled by a number of factors, governing interactions between organic and inorganic substructures. The principles that describe these interactions include hydrophillic–hydrophobic interactions, charge-density matching and weak hydrogen bonding that nevertheless may induce distortions of particular geometries of U–O–Se links. Herein we report on the syntheses and structural characterization of seven novel Se-contaning uranyl oxysalts that contain protonated organic molecules as interlayer species.

2. Experimental

2.1. Synthesis

N,*N*-dimethylformamide (99%, Sigma-Aldrich), dimethylamine (40 wt% in H_2O, Aldrich), diethylenetriamine (99%, Sigma-Aldrich), diethylamine (99%, Sigma-Aldrich), selenic acid (40 wt% in H_2O, 99.95%, Aldrich), and $UO_2(NO_3)_2 \cdot 6H_2O$ (Vekton) were used as received. $[C_2H_8N]_2[(UO_2)(SeO_4)_2(H_2O)]$ (**I**), $[C_2H_8N]_2[(UO_2)_2(SeO_4)_3(H_2O)]$ (**II**), $[C_4H_{15}N_3][H_3O]_{0.5}[(UO_2)_2(SeO_4)_{2.93}(SeO_3)_{0.07}(H_2O)](NO_3)_{0.5}$ (**III**), $[C_2H_8N]_3[H_5O_2][(UO_2)_2(SeO_4)_3(H_2O)_2]_2(H_2O)_5$ (**IV**), $[C_2H_8N]_2[H_3O][(UO_2)_3(SeO_4)_4(HSeO_3)(H_2O)](H_2SeO_3)_{0.2}$ (**V**), $[C_4H_{12}N]_3[H_3O][(UO_2)_3(SeO_4)_5(H_2O)]$ (**VI**), and $[C_2H_8N]_3(C_2H_7N)[(UO_2)_3(SeO_4)_4(HSeO_3)(H_2O)]$ (**VII**) have been prepared by evaporation from aqueous solutions of uranyl nitrate, 40%—solution of selenic acid, *N*,*N*-dimethylformamide, 40%—solution of methylamine, diethylenetriamine, diethylamine, and deionized distilled water. Yellow–green homogeneous liquid solutions were left in a fumehood at the room temperature. The crystals of compound **I**, and **II** were synthesized through the reaction 0.198 g (0.4 mmol) of uranyl nitrate, 0.094 g (1.3 mmol) of *N*,*N*-dimethylformamide,

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0.590 g (4.1 mmol) of selenic acid and 2.001 g (110.2 mmol) of deionized distilled water. The crystals of compound **IV**, and **V** were synthesized through the reaction 0.0502 g (0.1 mmol) of uranyl nitrate, 0.009 g (0.2 mmol) of dimethylamine, 0.102 g (0.7 mmol) of selenic acid and 2.002 g (110.2 mmol) of deionized distilled water. The crystals of compound **VII** were synthesized through the reaction 0.0502 g (0.1 mmol) of uranyl nitrate, 0.018 g (0.4 mmol) of dimethylamine, 0.072 g (0.5 mmol) of selenic acid and 2.001 g (110.2 mmol) of deionized distilled water. The crystals of compound **III** were synthesized through the reaction 0.100 g (0.2 mmol) of uranyl nitrate, 0.010 g (0.1 mmol) of diethylenetriamine, 0.102 g (0.7 mmol) of selenic acid and 2.002 g (110.2 mmol) of deionized distilled water. The crystals of compound **VI** were synthesized through the reaction 0.059 g (0.1 mmol) of uranyl nitrate, 0.010 g (0.1 mmol) of diethylamine, 0.679 g (4.7 mmol) of selenic acid and 2.002 g (110.2 mmol) of deionized distilled water. The solid products were formed after three days in small amount. The pH values of the solutions described above are in the range from 1 to 0, moreover for the newly prepared solutions the values tend closer to 1, whereas precipitation of crystals increases acidity.

2.2. *Single crystal X-ray study*

Single crystals of **I–VII** have been selected for data collection under an optical microscope, encased in epoxy and mounted on glass fibres. Data were collected using monochromatic Mo*K*α radiation (λ[Mo*K*α]= 0.71073 Å) by means of a Bruker SMART APEX II CCD (**I–VI**) and STOE IPDS II (**VII**) diffractometers. The unit-cell parameters were refined by least-squares techniques. Data were integrated and corrected for background, Lorentz, and polarization effects using an empirical spherical model by means of the Bruker programs *APEX2* and *XPREP* (**I–VI**) and *STOE X-AREA* (**VII**). Absorption correction was applied using the *SADABS* program [25] for (**I–VI**) and *STOE X-RED* & *X-SHAPE* [26] for **VII**. The structures were solved by direct methods and refined using the SIR-92 [27] and *SHELXL*-97 programs [28] incorporated in the *OLEX2* program package [29]. Due to the low quality of crystals (especially phases **IV–VII**), their metastability and sensitivity to air, only rather rough structural models could be obtained, which is manifested in the presence of high residual electron-density peaks, low bond precision, and refinement of organic molecules in isotropic approximation only (**VII**), as well as in the impossibility to localize the positions of several H atoms. However, the hydrogen bonding system in such cases can be inferred from the short O–O contacts involving sites occupied by water and hydronium molecules. 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 1.5U_{eq}(C) and C–H 0.96 Å for CH_3 groups, with U_{iso}(H) set to 1.2U_{eq}(C) and C–H 0.97 Å for CH_2 groups, U_{iso}(H) set to 1.2U_{eq}(N) and N–H 0.89 Å for the NH_3 groups, and U_{iso}(H) set to 1.2U_{eq}(N) and N–H 0.86 Å for the NH_2 groups. Positions of H atoms of H_2O molecules, hydronium cations and OH^- groups were localized from difference Fourier maps and kept fixed during refinement. Relevant crystallographic data are listed in Table 1. Selected interatomic distances are listed in Tables S1–S7. CCDC files 901940, 901941, 901942, 901943, 901944, 901945, and 901946 contain the supplementary crystallographic data for the compounds **I–VII**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

3. Results

3.1. *Structural descriptions*

The crystal structures of all seven compounds reported in this paper contain uranyl pentagonal bipyramids and selenate tetrahedra. The structures of **V** and **VII** also contain selenite trigonal pyramids. The polyhedra are linked into inorganic structural units. The structures contain one (**I**), two (**II**, **III**, **V**, **VI** and **VII**), or four (**IV**) crystallographically unique U^{VI} cations forming approximately linear uranyl ions, $[UO_2]^{2+}$, with the U=O bond lengths varying from 1.711(10) Å to 1.787(7) Å. These basic uranyl entities are coordinated in their equatorial planes by four oxygen atoms and one H_2O molecule to form UO_7 pentagonal bipyramids with the average $\langle$U–O$_{eq}\rangle$ bond lengths equal to 2.390 Å. The U–H_2O bond lengths lie in range of 2.424(12)–2.554(7) Å. In the structure of **I** there are two symmetrically independent Se^{VI} atoms. The structures of **II**, **III**, **IV**, and **VI** contain three Se^{VI} atoms each, whereas the structure of **IV** contains six

Table 1
Crystallographic data for **I**, **II**, **III**, **IV**, **V**, **VI** and **VII**.

Compound	**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**
Formula mass	666.15	1079.14	2256.03	2267.28	1685.05	1770.70	1685.07
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	$P2_1/m$	$P2_1/m$	*Pnma*
a (Å)	7.5363(7)	11.2154(5)	11.1679(4)	12.451(5)	8.3116(4)	8.941(2)	11.6591(11)
b (Å)	12.2021(11)	11.2263(5)	10.9040(4)	31.126(5)	18.6363(8)	19.300(4)	14.9556(17)
c (Å)	16.7601(16)	16.9138(8)	17.9913(6)	14.197(4)	11.5623(5)	11.377(3)	22.194(2)
β (°)	90.00	90.00	98.019(1)	120.39(2)	97.582(1)	97.510(4)	90.00
V (Å^3)	1541.2(2)	2129.57(17)	2169.57(17)	4746(2)	1775.31(14)	1946.5(7)	3870.0(7)
Size (mm^3)	0.21 × 0.17 × 0.09	0.21 × 0.17 × 0.07	0.23 × 0.19 × 0.08	0.23 × 0.18 × 0.07	0.19 × 0.14 × 0.08	0.22 × 0.20 × 0.06	0.26 × 0.20 × 0.09
μ (mm^{-1})	15.306	20.394	20.036	18.323	19.286	17.217	17.310
Z	4	4	2	4	2	2	4
2θ range (°)	4.13–60.00	4.35–60.00	4.38–55.00	2.62–55.00	4.17–60.00	4.18–54.98	3.28–39.10
D_{calc} (g/cm^3)	2.871	3.366	3.457	3.173	3.152	3.021	2.892
Total ref.	13,644	17,184	23,671	34,682	23,753	18,435	10,911
Unique ref.	4492	6112	4988	10896	5323	4597	1680
Unique $\lvert F_o\rvert \geq 4\sigma_F$	4117	5340	3855	5379	3940	2459	1221
R_{int}	0.0564	0.0651	0.0723	0.0963	0.0762	0.1196	0.1116
R_σ	0.0562	0.0684	0.0574	0.0993	0.0605	0.1609	0.0714
R_1 ($\lvert F_o\rvert \geq 4\sigma_F$)	0.0311	0.0283	0.0330	0.0482	0.0362	0.0396	0.0602
wR_2 ($\lvert F_o\rvert \geq 4\sigma_F$)	0.0629	0.0484	0.0735	0.1060	0.0935	0.0583	0.0962
GOF	0.940	0.934	0.964	0.875	1.083	0.737	1.127
ρ_{min}, ρ_{min}, e (Å^3)	−1.497, 2.339	−1.199, 1.099	−1.997, 2.824	−4.340, 4.608	−2.216, 2.793	−1.383, 1.651	−1.210, 1.054
CCDC	901940	901941	901942	901943	901944	901945	901946

Note: $R_1=\Sigma\lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$; $wR_2=\{\Sigma\ [w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$, where $P=(F_o^2+2F_c^2)/3$; $\mathrm{GOF}=\{\Sigma[w(F_o^2-F_c^2)]/(n-p)\}^{1/2}$ where n is the number of reflections and p is the number of refined parameters.