Self-Assembly of Protonated 1,12-Dodecanediamine Molecules and Strongly Undulated Uranyl Selenate Sheets in the Structure of Amine-Templated Uranyl Selenate: $(H_3O)_2[C_{12}H_{30}N_2]_3[(UO_2)_4(SeO_4)_8](H_2O)_5$

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The amine-templated uranyl selenate $(H_3O)_2[C_{12}H_{30}N_2]_3[(UO_2)_4(SeO_4)_8](H_2O)_5$ (**1**) has been prepared. Its structure [monoclinic, $P2_1/n$, a = 11.3437(7), b = 24.8042(12), c = 29.2496(19) Å, β = 96.701(5)°, V = 8173.8(8) Å^3, Z = 4, R_1 = 0.083] is based upon strongly undulating $[(UO_2)(SeO_4)_2]^{2-}$ sheets consisting of corner-sharing UO_7 bipyramids and SeO_4^{2-} tetrahedra. The undulations of the adjacent sheets have an *anti*-phase character that allows the formation of large eliptical channels that are occupied by rod micelles formed by self-assembly of protonated 1,12-dodecanediamine molecules.

Introduction

The preparation of new porous uranium-based materials is of interest because of their relevance to radioactive waste disposal, utilization of depleted uranium, catalysis, etc.[1] One of the pathways employed in the synthesis of new compounds is the use of amines as templates.[2] The role of amines as structure-directing agents has been under extensive discussion. There are strong indications that, in some systems, amine molecules may control the formation of new topologies that are not observed in purely inorganic structures, whereas in other systems the role of protonated amine molecules is simply to balance the negative charge of the inorganic part of a structure.[2] We note that in the preparation of uranium-based oxide compounds, short-chain and cyclic amines have mostly been employed, whereas the effect of long-chain amines, especially α,ω-alkyldiamines, is as yet unknown. We report here the synthesis and structure of $(H_3O)_2[C_{12}H_{30}N_2]_3[(UO_2)_4(SeO_4)_8](H_2O)_5$ (**1**), a new uranyl selenate templated by 1,12-dodecanediamine molecules.

Whereas the structural chemistry of uranyl selenites has been intensively investigated over the last few years,[2f,3] uranyl selenates have received much less attention[4] as their synthesis under low-temperature hydrothermal conditions (100–250 °C) rarely results in crystalline selenates, even if selenic acid, H_2SeO_4, is used as a source of selenium. This is caused by the instability of the selenate ion, SeO_4^{2-}, and its easy reduction to selenite, SeO_3^{2-}.[2f,5] To avoid the selenate/selenite reduction, yellow needles of **1** have been prepared by room-temperature evaporation of the solvent from an aqueous solution of uranyl nitrate, selenic acid, and 1,12-dodecanediamine. A semi-quantitative EDX analysis indicated a U/Se ratio of 1:2, and a single-crystal X-ray diffraction experiment allowed the crystal-structure characterization. The results of IR spectroscopic studies were found to be in good agreement with the results of the crystal-structure investigations.

Results and Discussion

The structure of **1** consists of well-defined organic and inorganic substructures (Figure 1). The inorganic substructure contains four symmetrically independent U^{VI} centers that form linear uranyl cations, UO_2^{2+} (U=O distances in the range of 1.732–1.766 Å). These uranyl cations are further coordinated equatorially by five oxygen atoms each to form pentagonal UO_7 bipyramids (U–O 2.326–2.500 Å). There are eight symmetrically independent Se^{VI} cations, each tetrahedrally coordinated by four oxygen atoms (Se–O 1.597–1.671 Å). The bond-valence sums for the U and Se atoms[6] are in the range of 5.89–6.35 valence units (v.u.). The UO_7 bipyramids and SeO_4^{2-} tetrahedra share corners to form the $[(UO_2)(SeO_4)_2]^{2-}$ sheets depicted in Figure 2 (see a). These sheets are parallel to (001) and are strongly undulated along the *c* axis. The undulation vector is parallel to [010] and is equal to *b* (24.804 Å). The undulation amplitude is about 25 Å. The undulations in the adjacent sheets

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have an *anti*-phase character which means that large eliptical channels are created along the *a* axis.

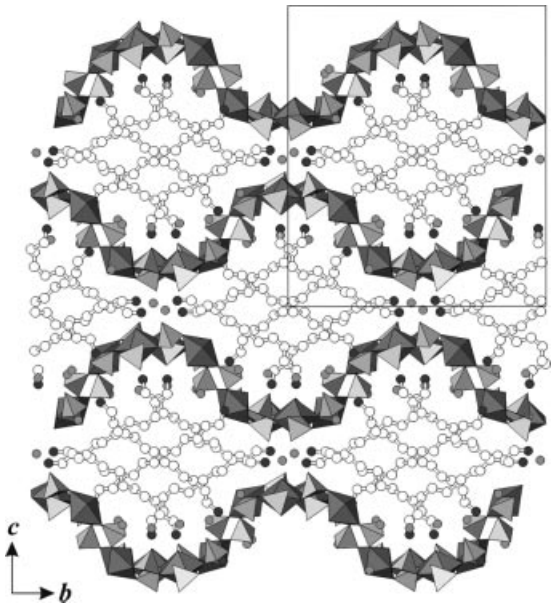

Figure 1. Crystal structure of **1** projected along the *a* axis. $[UO_7]^{8-}$ bipyramids are dark grey, and $[SeO_4]^{2-}$ tetrahedra are light grey. C and N atoms, and H_2O groups are shown as white, dark grey and light grey circles, respectively.

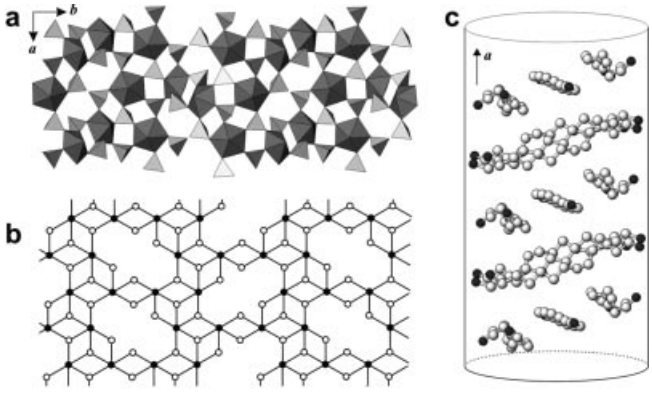

Figure 2. The $[(UO_2)(SeO_4)_2]^{2-}$ sheet in the structure of **1** (a), nodal representation (U and Se polyhedra are symbolized by black and white circles, respectively) (b), and organization of 1,12-dodecanediamine molecules into a rod micelle (c).

The topology of the $[(UO_2)(SeO_4)_2]^{2-}$ sheets is remarkable as it has not been observed previously in any uranium compound. It can be analyzed by means of a nodal representation, which is especially suitable for the description of structures based upon coordination polyhedra of two types.[7] Using this approach, the UO_7 bipyramids and SeO_4 tetrahedra are symbolized by black and white vertices, respectively. The vertices are linked by a line segment if two respective polyhedra share a common oxygen atom. The idealized black-and-white graph of the uranyl selenate sheet observed in **1** is shown in Figure 2 (see b). Although it is new for uranium chemistry, it can be obtained from a more regular (3.6.3.6) graph by eliminating some of its vertices and edges. This topological procedure is common for many sheet topologies observed in uranyl oxo salts.[2c,7]

The organic substructure consists of micelles of protonated 1,12-dodecanediamine molecules oriented parallel to the *a* axis. These micelles occupy the channels created by the packing of the $[(UO_2)(SeO_4)_2]^{2-}$ sheets. The assembly scheme of the 1,12-dodecanediamine chain molecules within the micelle is shown in Figure 2 (see c). The molecules are arranged into sublayers approximately parallel to (–102). The planes of these sublayers are not perpendicular to the micelle axis but form an angle of about 60°. In each layer, there are three parallel oriented $[C_{12}H_{30}N_2]^{2+}$ molecules. The molecules in the adjacent layers are at an angle of 30° relative to each other, which results in the elliptical form of the perpendicular section of the micelle. The lateral dimensions of the micelle are about 20 × 24 Å, i.e. are at the level of nanometers. The interactions between organic and inorganic substructures involve N···O hydrogen bonds to oxygen atoms of uranyl ions and terminal oxygen atoms of selenate tetrahedra. In addition, the structure contains two symmetrically independent H_3O^+ ions and five symmetrically independent H_2O molecules that contribute to the network of hydrogen bonds. The H_3O^+ ions correspond to the O(41) and O(42) sites, which can easily be identified as oxoniums by the analysis of their coordination environment. Both O(41) and O(42) are coordinated to three oxygen atoms located at O···O distances of 2.47–2.64 Å (Table 1). This coordination is a rather flat pyramid that can be inferred from the O···H_3O···O angles of 99.0–123.8°. This coordination geometry is typical for oxonium ions in oxo salt structures and has been observed in the structures of $(H_3O)(HSeO_4)$,[8] $(H_3O)(HSO_4)$,[9] $M(H_3O)(HSO_4)_2$ (M = Na,[10] K,[11] Ag[12]), $(H_3O)Sb_2(SO_4)_2$,[13] $Zr(H_3O)_2(SO_4)_3$,[14] $(H_3O)La(SO_4)_2(H_2O)$,[15] $(H_5O_2)(H_3O)_2Nd(SO_4)_3$,[16] $(H_3O)_2Nd(HSO_4)_3(SO_4)$,[16] etc. There are also several oxonium uranyl selenate hydrates known, although the coordination geometries of the oxonium ions in their structures are not as well-defined as in the structure of **1**. The presence of oxonium in **1** can also be confirmed by the presence of a strong band at 2853 cm^{-1} in the IR spectrum of **1**. This band can be assigned to strong hydrogen bonds corresponding to O···O distances of about 2.5–2.6 Å[17] (compare with the distances given in Table 1).

Protonated long-chain amine molecules are known to form cylindrical micelles in aqueous solutions by a self-assembly process that is governed by competing hydrophobic/hydrophilic interactions.[18] The flexible inorganic complexes present in the reaction mixture could then form around these cylindrical micelles to produce an inorganic structure that reflects the cylindrical form of the micelles. In the case of **1**, the inorganic structure has the form of a strongly undulated sheet, although structures with highly porous uranyl selenate nanotubules have also been observed.[19] This indicates the possibility of preparation of uranium oxo salt mesostructures if larger organic moieties (e.g., block copolymers) are involved in the synthesis procedure. This possibility is favored by the high flexibility of

Table 1. Selected interatomic distances [Å] for $(H_3O)_2[C_{12}H_{30}N_2]_3[(UO_2)_4(SeO_4)_8](H_2O)_5$ (**1**).

U(1)–O(6)	1.734(12)	U(3)–O(21)	1.733(14)
U(1)–O(3)	1.759(13)	U(3)–O(38)	1.741(13)
U(1)–O(1)	2.362(11)	U(3)–O(10)	2.326(13)
U(1)–O(4)	2.383(13)	U(3)–O(24)	2.331(17)
U(1)–O(25)	2.387(11)	U(3)–O(33)	2.379(13)
U(1)–O(30)	2.395(13)	U(3)–O(11)	2.431(12)
U(1)–O(15)	2.405(12)	U(3)–O(12)	2.468(12)
U(2)–O(27)	1.754(12)	U(4)–O(16)	1.745(12)
U(2)–O(22)	1.766(11)	U(4)–O(2)	1.758(12)
U(2)–O(39)	2.333(12)	U(4)–O(7)	2.367(12)
U(2)–O(17)	2.343(11)	U(4)–O(23)	2.384(11)
U(2)–O(20)	2.379(12)	U(4)–O(26)	2.405(13)
U(2)–O(29)	2.416(11)	U(4)–O(14)	2.423(12)
U(2)–O(18)	2.502(12)	U(4)–O(28)	2.429(11)
Se(1)–O(17)	1.628(11)	Se(5)–O(13)	1.614(13)
Se(1)–O(10)	1.630(13)	Se(5)–O(33)	1.623(13)
Se(1)–O(32)	1.631(12)	Se(5)–O(15)	1.634(12)
Se(1)–O(28)	1.633(11)	Se(5)–O(18)	1.648(12)
Se(2)–O(9)	1.602(13)	Se(6)–O(24)	1.601(17)
Se(2)–O(39)	1.626(12)	Se(6)–O(19)	1.612(14)
Se(2)–O(14)	1.630(12)	Se(6)–O(1)	1.635(12)
Se(2)–O(12)	1.639(12)	Se(6)–O(20)	1.643(12)
Se(3)–O(34)	1.624(13)	Se(7)–O(40)	1.609(15)
Se(3)–O(25)	1.628(11)	Se(7)–O(8)	1.627(16)
Se(3)–O(35)	1.631(14)	Se(7)–O(30)	1.646(13)
Se(3)–O(11)	1.638(12)	Se(7)–O(7)	1.660(12)
Se(4)–O(5)	1.626(12)	Se(8)–O(36)	1.598(17)
Se(4)–O(37)	1.635(13)	Se(8)–O(26)	1.617(13)
Se(4)–O(23)	1.649(11)	Se(8)–O(31)	1.620(18)
Se(4)–O(29)	1.672(11)	Se(8)–O(4)	1.633(13)
$H_3O(41)$–O(5)	2.604(17)	$H_3O(42)$–O(31)	2.44(2)
$H_3O(41)$–O(8)	2.47(2)	$H_3O(42)$–O(34)	2.639(19)
$H_3O(41)$–O(35)	2.554(19)	$H_3O(42)$–O(37)	2.584(19)

the U–O–T links in uranyl compounds with tetrahedral TO_4^{2-} anions (T = S, Cr, Se, Mo).[20] The fabrication of meso- and nanostructures in uranium oxo-systems might be of great interest for the preparation of new functional nanomaterials and their subsequent use in nanotechnology. The latter perspective seems to be a promising direction for the utilization of depleted uranium, thousands tons of which are now stored in countries such as the USA and Russia.

Experimental Section

In a typical synthesis of **1**, 0.028 g of 1,12-dodecanediamine, 0.30 mL of 40% H_2SeO_4, and 0.081 g of $(UO_2)(NO_3)_2{\cdot}6H_2O$, were mixed with 2 mL of distilled H_2O. The mixture was poured into a watch glass and was kept in a fume hood at room temperature. Yellow needles of **1** were formed in approximately 10% yield (0.008 g) in about 3–4 days. The compound was characterized by semi-quantitative electron microprobe analysis. Far-IR and Raman spectra were recorded and the presence of uranyl ions and selenate groups was confirmed. Far-IR (nujol): $\tilde{\nu}$ = 3566 (m), 3486 (s), 3155 (m), 2927 (s), 2853 (s), 1613 (s), 1505 (m), 1470 (w), 1211 (w), 1191 (w), 1150 (w), 1016 (vw), 954 (s), 919 (m), 888 (s), 848 (s), 822 (s), 725 (m) cm^{-1}.

Crystallographic Data for $(H_3O)_2[C_{12}H_{30}N_2]_3[(UO_2)_4(SeO_4)_8](H_2O)_5$: Plate-like crystal ($0.02\times0.04\times0.22\ mm^3$), monoclinic, $P2_1/n$, a = 11.3437(7), b = 24.8042(12), c = 29.2496(19) Å, β = 96.701(5)°, V = 8173.8(8) $Å^3$, Z = 4, ρ_{calc} = 2.405 $g\,cm^{-3}$, $2\theta_{max}$ = 54.28°, λ(Mo-K_α) = 0.71073 Å, ω-scan (1° per image) at φ = 0° (STOE IPDS II), 293 K, 48 038 measured reflections, 17023 independent reflections, 11646 reflections with $|F_o| \geq 4\sigma_F$ (R_{int} = 0.084, R_σ = 0.089), numerical absorption correction (programs X-Shape and X-Red, STOE, Darmstadt, 1998), structure solution by direct methods, full-matrix least-square refinement (263 parameters) on $|F^2|$, no treatment of H atoms [programs SIR-97[21] and SHELXL-97 (G. M. Sheldrick, program for the refinement of crystal structures, Göttingen, **1997**)], R_1 = 0.083, wR_2 = 0.137 for observed reflections, max./min. electron density = 2.703/–1.672.

CCDC-261122 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data via www.ccdc.cam.ac.uk/data_request/cif.

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