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A Crown Ether as Template for Microporous and Nanostructured Uranium Compounds**

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Microporous and nanostructured actinide compounds are of great interest due to their formation during alteration of spent nuclear fuel and their potential applications in the nuclear industry and radiochemistry.[1] Synthesis of these compounds usually involves addition of organic templates, such as amines, with different shapes and compositions.[1a–d,2] Herein we report on the syntheses and structures of two unusually complex, highly porous uranyl compounds which contain sulfate or selenate and are templated by the [18]crown-6 complex of the hydronium ion H_3O^+.

Yellow transparent crystals of $(H_3O)_8[(H_3O)@([18]\text{crown-6})]_2[(UO_2)_{14}(SO_4)_{19}(H_2O)_4](H_2O)_{20.5}$ (**1**) and $(H_3O)_2K[(H_3O)@([18]\text{crown-6})][(UO_2)_3(SeO_4)_5](H_2O)_4$ (**2**) were obtained by evaporation from aqueous solutions of uranyl nitrate, [18]crown-6, and sulfuric or selenic acid.[3] The structures of both compounds[4,5] contain U^{6+} ions in uranyl ions $[O{=}U{=}O]^{2+}$ that are coordinated by five additional O atoms in their equatorial planes. The resulting UO_7 pentagonal bipyramids share corners with $[TO_4]^{2-}$ tetrahedral oxo anions (T = S, Se) to produce unique and highly porous structural units.

The structure of **1** (Figure 1) consists of an exceptionally complex $[(UO_2)_{14}(SO_4)_{19}(H_2O)_4]^{10-}$ microporous framework with a low framework density (FD) of 8.5 M atoms per 1000 Å^3, where M is a framework-forming cation, that is, U and S; for comparison, the open zeolite faujasite has FD ≈ 13.5. The framework has large cross-shaped channels running parallel to the *c* axis. The channels are formed by rings of 16 M-centered polyhedra and are occupied by the water molecules and $[(H_3O)@([18]\text{crown-6})]^+$ complexes. The channels have absolute dimensions of 8.8 × 8.8 Å, which correspond to crystallographic free dimensions of 6.1 × 6.1 Å (assuming oxygen radii of 1.35 Å). The largest cavity of the framework is centered approximately at $(^1/_2{}^1/_2{}^1/_2)$ and has the form of a flattened disk with approximate dimensions of 20 × 20 × 8 Å. As far as we know, this is the highest porosity ever observed for an actinide-based oxide microporous framework structure. The previous record was FD = 9.1 M/1000 Å^3 and largest channel dimensions of 4.8 × 4.8 Å[1b] for the uranyl molybdate framework in $(NH_4)_4[(UO_2)_5(MoO_4)_7](H_2O)_5$. The $[(H_3O)@([18]\text{crown-6})]^+$ complexes have typical geometries with the H_3O^+ ion at the center of the crown ether and $H_3O^+\cdots O$ distances of 2.65–2.66 Å.[6] Additional hydronium ions are located in the framework and form hydrogen bonds to the O atoms of uranyl and sulfate polyhedra. These H_3O^+ ions have threefold coordination of O atoms and H_2O groups, as previously observed in uranyl compounds.[7]

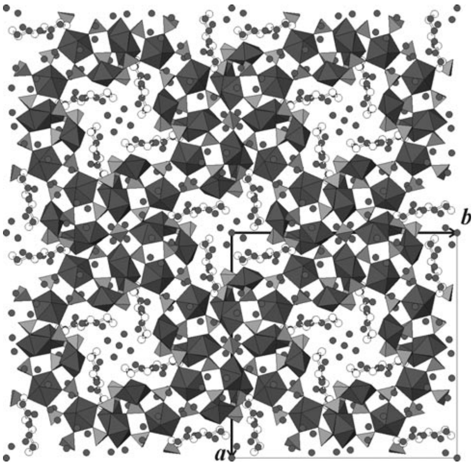

Figure 1. Crystal structure of **1** projected along the *c* axis. U and S polyhedra are dark gray and light gray, respectively; H_2O and H_3O^+ are gray; C atoms are white.

The topology of the uranyl sulfate framework can be conveniently described with graph theory by replacing U and S coordination centers by black and white nodes, respectively, and linking those nodes that correspond to polyhedra sharing a common anion.[8] The resulting three-dimensional (3D) graph is shown in Figure 2a. It can be described as consisting of 2D nets formed by nodes corresponding to the U1, U2, U4, S1, S2, S3, S5, and S6 coordination centers (Figure 2b) linked in the third dimension by the nodes corresponding to the U3 and S4 centers. This topology is unprecedented in actinide structural chemistry and in oxo salt chemistry in general.[9]

The structure of **2** consists of $[(UO_2)_3(SeO_4)_5]^{4-}$ uranyl selenate nanotubules that extend along the *a* axis and are identical to those found in $K_5[(UO_2)_3(SeO_4)_5](NO_3)(H_2O)_{3.5}$ (**3**).[1i] However, in contrast to the structure of **3**, in which the analogous tubules are packed according to a hexagonal packing of rods, in the structure of **2** the tubules form a

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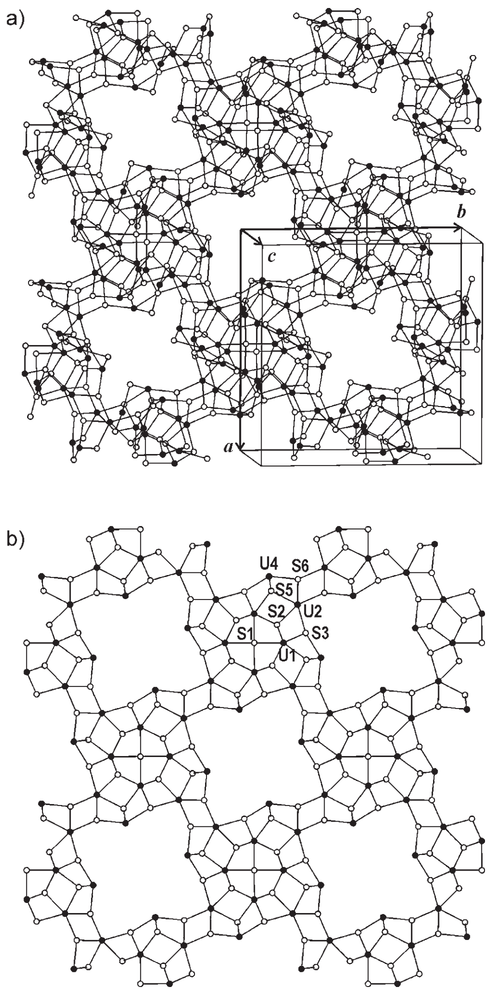

Figure 2. 3D black-and-white graph corresponding to the topology of polyhedral linkages in the structure of **1** (a) and 2D graph of uranyl sulfate layered substructure (b). U and S coordination centers are shown as black and white circles, respectively. See text for details.

tetragonal packing, as they are separated by columns of disordered $[(H_3O)@([18]crown\text{-}6)]^+$ complexes (Figure 3). Analogously to **3**, the internal space of the $[(UO_2)_3(SeO_4)_5]^{4-}$ tubules is filled by K^+ ions and H_2O molecules. Both topological and isomeric features of the tubules in **2** are identical to those of the tubules in **3**. The external diameter of the tubule is 17 Å, while its internal diameter, measured as the distance between the closest oxygen atoms, is 7.4 Å. The crown ether complexes of H_3O^+ in **2** separate the uranyl selenate tubules from one another.

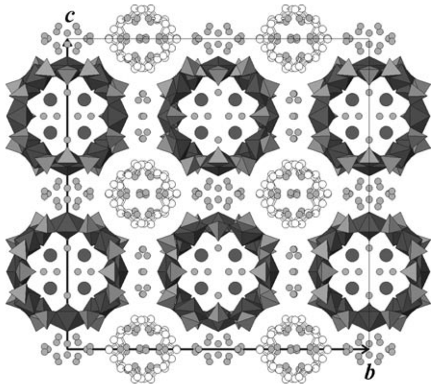

Figure 3. Crystal structure of **2** projected along the *a* axis. U and Se polyhedra are dark gray and light gray, respectively; H_2O and H_3O^+ are gray; C atoms are white.

In both structures, the uranyl ions have coordination geometries typical for uranyl compounds.[9] The U=O distances are in the range of 1.74–1.78 and 1.74–1.80 Å for **1** and **2**, respectively, while equatorial U−O bond lengths are 2.34–2.48 and 2.35–2.48 Å for **1** and **2**, respectively. The T−O_{br} bonds to O_{br} atoms bridging between U and T centers are generally longer than those to terminal O_{term} atoms in the $[TO_4]^{2-}$ tetrahedra (S−O_{br} 1.43–1.49, S−O_{term} 1.43–1.44 Å for **1**; Se−O_{br} 1.617–1.704, Se−O_{term} 1.581–1.641 Å for **2**). The U-O_{br}-S bond angles in **1** exhibit rather broad variation, from 129.3 to 162.0°, whereas the range of U-O_{br}-Se bond angles in **2** is much narrower (125.4–143°). The difference in the ranges of bond angles reflects surprisingly high flexibility of uranyl sulfate networks in comparison to uranyl selenate networks that allows easier formation of 3D topologies.

In conclusion, synthesis and characterization of **1** and **2** demonstrate new possibilities for engineering novel microporous and nanotubular actinide topologies by using large organic cations such as a crown ether complex of the hydronium ion.

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[3] Synthesis of **1**: H_2SO_4, [18]crown-6, and $UO_2(NO_3)_2(H_2O)_2$ (molar ratio 2:1.5:1) were dissolved in distilled water (25 mL), and the solution was left to evaporate at room temperature in air. Yellow transparent crystals of **1** formed after 10 d. Synthesis of **2**: $UO_2(NO_3)_2(H_2O)_2$ (0.05 g), [18]crown-6 (0.008 g), KNO_3 (0.005 g), and H_2SeO_4 (0.06 mL, 40 %) were dissolved in distilled water (5 mL). The solution was left to evaporate at room temperature in air. Elongated greenish crystals of **2** formed after 5 d. In the IR spectrum of **1**, the most intense bands are in the ranges of 3600–2850 and 1616–457 cm^{-1}: 3590 and 3529 (ν(OH) of H_2O); 3368 (ν(OH) of H_3O^+); 2899 (ν_s(CH) of [18]crown-6); 1616 (δ of H_2O), 920 (linear UO_2^{2+} groups); 457, 600, 636, and 961 (SO_4 tetrahedra); 1000, 1057, 1103, 1203, 1348, and 1456 cm^{-1} ([18]crown-6).

[4] Crystallographic data for $(H_3O)_8((H_3O)@[C_{12}H_{24}O_6])_2[(UO_2)_{14}(SO_4)_{19}(H_2O)_4]\cdot 20.5\,H_2O$ (**1**): transparent blocklike crystal, 0.20 × 0.20 × 0.10 mm, tetragonal, *I*4*m*, $a = 28.023(1)$, $c = 19.6840(7)$ Å, $V = 15457.6(10)$ Å^3, $Z = 2$; $\rho_{calcd} = 2.724\ g\,cm^{-3}$, $2\theta_{max} = 56°$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å; ϕ scan (Mar345 Image Plate), 293 K, 64196 measured reflections, 9499 independent reflections, 8905 reflections with $|F_o| \geq 4\sigma_F$ ($R_{int} = 0.0567$, $R_\sigma = 0.0337$), structure solution by direct methods, full-matrix least-squares refinement (404 parameters) on $|F^2|$, programs SHELXS-97 and SHELXL-97 (G. M. Sheldrick, Program for the refinement of crystal structures, Göttingen, **1997**), $R_1 = 0.0520$, $wR_2 = 0.1035$ for observed reflections, $R_1 = 0.0575$, $wR_2 = 0.1058$ for all data, max./min. electron density 1.587/−1.515.

[5] Crystallographic data for $(H_3O)_2K[(H_3O)@[C_{12}H_{24}O_6]][(UO_2)_3(SeO_4)_5](H_2O)_4$ (**2**): transparent elongated crystal, 0.12 × 0.16 × 0.24 mm, orthorhombic, *Ccmm*, $a = 11.292(1)$, $b = 37.158(1)$, $c = 38.504(1)$ Å, $V = 16155.8(16)$ Å^3, $Z = 16$, $\rho_{calcd} = 3.219\ g\,cm^{-3}$; $2\theta_{max} = 52.74°$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, ϕ scan (Mar345 Image Plate), 293 K, 52358 measured reflections, 8350 independent reflections, 7951 reflections with $|F_o| \geq 4\sigma_F$ ($R_{int} = 0.0910$, $R_\sigma = 0.0523$), structure solution by direct methods, full-matrix least-squares refinement (433 parameters) on $|F^2|$, programs SHELXS-97 and SHELXL-97 (G. M. Sheldrick, Program for the refinement of crystal structures, Göttingen, **1997**), $R_1 = 0.0850$, $wR_2 = 0.1616$ for observed reflections, $R_1 = 0.0898$, $wR_2 = 0.1690$ for all data, max./min. electron density 3.171/−3.249. CCDC 639414 (**1**) and CCDC 639415 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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