Communication

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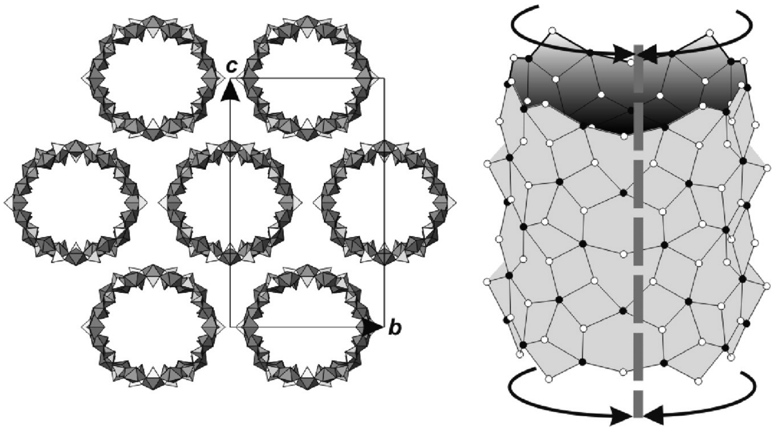

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Highly Porous Uranyl Selenate Nanotubules

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Since the discovery of carbon nanotubes in 1991,[1] a great deal of attention was attracted to inorganic nanotubes as promising modules for nanotechnology applications.[2] Oxidic nanotubes are of special interest because of their unique atomic structure and interesting physical properties.[3] Most of the synthesized nanotubes in oxide systems possess lamellar structures and can be considered as 2D nanosheets rolling into nanotubes or nanoscrolls.[4] Spontaneous formation of nanotubes was observed in a number of systems where exfoliation of lamellar solids into individual sheets can be achieved.[5] Thus, from a theoretical viewpoint, all layered structures with relatively weak bonding between the adjacent sheets can be transformed into tubular objects. Among inorganic compounds, sheet structures are especially characteristic for uranium(VI) oxocompounds due to the strong tendency of U^{6+} cations to form linear uranyl ions, UO_2^{2+}.[6] This determines high anisotropy of the U^{6+} coordination and favors formation of layers of coordination polyhedra.[7] Within the past decade, uranyl oxocompounds attracted considerable attention due to their importance for radioactive waste management, disposal of spent nuclear fuel, catalysis, etc. A large number of new compounds were characterized, including oxide−hydroxides,[8] phosphates,[9] selenites,[10] iodates,[11] molybdates,[12] sulfates,[13] chromates,[14] selenates,[15] tungstates,[16] silicates,[17] and so forth. Layered structures are dominant for these compounds, though 1D and 3D units have also been observed. However, no information is available about the possibility of formation of tubular objects in uranium-based systems, and little is known about nanostructures based upon uranium oxide. Here, we report synthesis and structure of $(C_4H_{12}N)_{14}[(UO_2)_{10}(SeO_4)_{17}(H_2O)]$ (**1**), a first amine-templated uranyl selenate based upon highly porous uranyl selenate nanotubules.

The yellow transparent crystals of **1** were obtained in the room-temperature reaction of uranyl nitrate, butylamine, and H_2SeO_4 in aqueous solution.[18] The crystals were found to be of quality and size suitable for an X-ray diffraction data collection. The structure of **1** was solved by direct methods.[19] It consists of nanometer-scale tubular $[(UO_2)_{10}(SeO_4)_{17}(H_2O)]^{14-}$ units oriented parallel to the *a* axis (Figure 1) and packed in a hexagonal-type fashion (Figure 2a). The tubules are single-layer and have elliptical cross section with outer dimensions of 25 × 23 Å = 2.5 × 2.3 nm. The internal diameter of the tubules measured as a distance between the closest oxygen atoms across the tubule is 15.3 Å that results in a free crystallographic diameter of 12.6 Å, that is, comparable to the effective pore size in large-pore zeolites[20] and close to the mesoporous size range.[21]

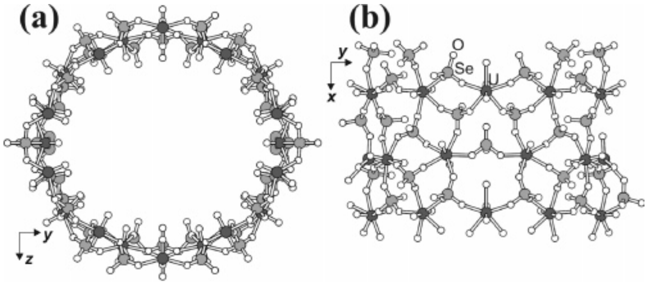

Figure 1. Ball-and-stick representation of the uranyl selenate nanotubule in the structure of **1**: (a) view parallel to the tubule axis; (b) fragment of the tubule wall approximately parallel to (001), showing coordination of U and Se atoms. Legend: U atoms = black, Se atoms = gray, O atoms = white.

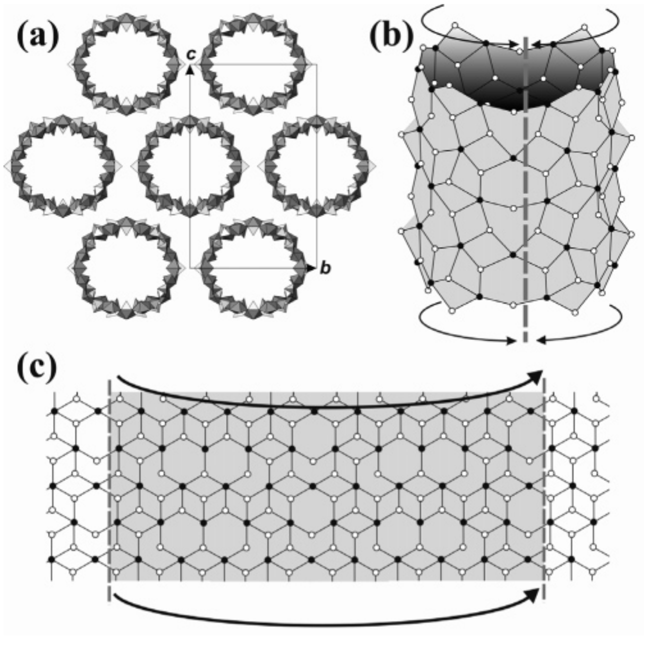

Figure 2. Crystal structure of **1** projected along [100] (a), black-and-white tubular graph corresponding to the topology of the uranyl selenate nanotubule in the structure of **1** (b), and unfolded version of this graph (c). $[UO_7]^{8-}$ bipyramids and $[SeO_4]^{2-}$ tetrahedra are symbolized by black and white vertexes, respectively.

The $[(UO_2)_{10}(SeO_4)_{17}(H_2O)]^{14-}$ nanotubules consist of UO_7 pentagonal bipyramids and SeO_4 tetrahedra sharing common oxygen atoms (Figure 1). The tubule sectors parallel to (001) are ordered, whereas the sectors parallel to (010) have a disordered structure. However, it was possible to localize disordered positions of the U and Se atoms in the (010) walls and thus to elucidate general structural features of the tubules. We were unable to determine positions of the C and N atoms inside the tubes due to their disordered arrangement.

Topological structure of the nanotubules can be described by means of a nodal representation, which is especially suitable for

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the description of structures based upon coordination polyhedra of two types.[22] Using this approach, the UO_7 bipyramids and SeO_4 tetrahedra are symbolized by black and white vertexes, respectively. The vertexes are linked by a line segment if two respective polyhedra share a common oxygen atom. The black-and-white graph corresponding to the topological structure of the $[(UO_2)_{10}(SeO_4)_{17}(H_2O)]^{14-}$ tubule is shown in Figure 2b. Its idealized unfolded version is given in Figure 2c. To obtain the tubular graph corresponding to the tubule shown in Figure 2b, one has to cut the graph into tapes along the lines indicated in Figure 2c, to fold the tape, and to glue its sides. The same procedure is applicable to most of inorganic nanotubes which can be (at least theoretically) obtained by exfoliation of single-layer sheets and their folding up into a tube. The 10:17 black-and-white graph shown in Figure 2c has not been observed previously as an underlying topology for any inorganic compound.

The mechanism of formation of uranyl selenate tubules in aqueous media is probably controlled by the presence of protonated butylamine $(C_4H_{12}N)^+$ cations. The protonated amine molecules with chain structure are known to form cylindrical micelles in aqueous solution that involves self-assembly governed by competing hydrophobic/hydrophilic interactions. The flexible uranyl selenate complexes present in the reaction mixture could then form around cylindrical micelles to produce an inorganic structure that reflects cylindrical form of the micelles. In the case of **1**, the inorganic structure has a form of a tubule, though structures with highly undulated uranyl selenate sheets have also been observed.

The most intense bands in the Raman and far-IR-spectra (see Supporting Information) can be assigned to vibrations of the uranyl cations (770, 880 cm^{-1}) and selenate tetrahedra (435, 830−840, 910−920 cm^{-1}). The bands between 1000 and 2000 cm^{-1}, as well as diffuse bands at ∼2900 and 3300−3400 cm^{-1}, are due to the presence of organic templates and water. TGA experiments show that the initial weight loss of 2−4% is observed between room temperature and 140 °C. The second weight loss is observed at 440 °C and corresponds to the total collapse of the structure.

In conclusion, we have succeeded in the preparation of highly porous uranyl selenate nanotubules, the first example of nanoscale structure containing uranium as a main structural component. This finding demonstrates the possibility of nanostructures for actinides in higher oxidation states. As layered structures are dominant for the U(VI) oxocompounds, we expect that a whole new range of uranium-based nanotubular materials can be fabricated. One possible application of these materials is the utilization of depleted uranium through its incorporation into nanomaterials for applications in nanotechnology. We also note that isolated nanotubules consisting of two types of coordination polyhedra represent a new type of structural unit in inorganic oxosalts with isolated tetrahedral oxoanions.

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Supporting Information Available: Crystallographic information file (CIF), additional structural information, and characterization data (IR and Raman spectra, TGA and DTA curves). This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) In a typical synthesis, 0.042 g of butylamine, 0.25 mL of 40% H_2SeO_4, and 0.086 g of $(UO_2)(NO_3)_2 \cdot 6H_2O$ were mixed with 2 mL of distilled H_2O and stirred until complete homogenization. The solution was poured into a watch glass and left to evaporate in a fumehood. Needlelike yellow crystals of **1** were formed in 90% yield in about 6−7 days. The U:Se ratio determined from semiquantitative EDX analysis is 10:17.8, which is close to the value 10:17 determined from crystal-structure analysis.

(19) Crystallographic data: platelike crystal (0.12 × 0.03 × 0.008 mm^3), orthorhombic, $I2mm$, $a = 10.8864(5)$, $b = 29.532(2)$, $c = 47.439(2)$ Å, $V = 15251.5(14)$ Å^3, $Z = 4$, $\rho_{calc} = 2.548$ g/cm^3, $2\theta_{max} = 49.84°$, λ(Mo Kα) = 0.71073 Å, ω-scan (1°/image) at $\varphi = 0$ and 90° (STOE IPDS II), 293 K, 48 132 measured reflections, 13 306 independent reflections, 11 304 reflections with $|F_o| \geq 4\sigma_F$ ($R_{int} = 0.090$, $R_\sigma = 0.061$), numerical absorption correction (programs X-Shape and X-Red, STOE, Darmstadt, 1998), structure solution by direct methods, full-matrix least-squares refinement (263 parameters) on $|F^2|$, no treatment of H atoms [programs SIR-97[24] and SHELXL-97 (Sheldrick, G. M. *Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997)], $R_1 = 0.083$, $wR_2 = 0.196$.

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