Oxidic Nanotubes

Nanoscale Tubules in Uranyl Selenates[**]

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Since the discovery of carbon nanotubes in 1991,[1] a great deal of attention has been devoted to the synthesis and characterization of inorganic nanotubes.[2] In particular, oxidic nanotubes exhibit interesting properties and hold promise for potential applications. Such nanotubes have been prepared for a variety of chemical systems, including vanadium oxides,[3] titania,[4] niobium oxides,[5] and rare-earth oxides.[6] One of the most accepted models of formation of nanotubes is the rolling and folding-up of single-layer sheets of the corresponding prototype lamellar materials.[2c,7] Thus, it is generally possible to prepare nanotubes and nanoscrolls from any lamellar material that can be exfoliated into separate nanosheets.[7] Among inorganic materials, layered structures are especially prevalent for hexavalent uranium oxo compounds[8] owing to the strong tendency of the U^{6+} ion to form linear uranyl ions, UO_2^{2+}. This tendency leads to a highly anisotropic distribution of chemical bonds within $\{U^{VI}O_n\}$ coordination polyhedra,[9] and, in particular, favors their condensation through longer U–O bonds lying in the equatorial plane relative to the uranyl ions. Despite the abundance of layered structures for U^{VI} oxo compounds, there are no reports of their ability to form tubular objects. Here, we report the synthesis and structure of $K_5[(UO_2)_3(SeO_4)_5](NO_3)(H_2O)_{3.5}$ (**1**), which is a new compound based upon nanoscale uranyl selenate tubules.

The uranyl selenate-nitrate **1** was obtained as small, greenish-yellow, transparent crystals (Figure 1) from the room-temperature reaction of uranyl nitrate, K_2CO_3, and H_2SeO_4 in aqueous solution.[10] The structure of **1**[11] was found to be highly unusual for inorganic oxo compounds with triangular and tetrahedral oxoanions such as NO_3^-, SeO_3^{2-}, SO_4^{2-}, SeO_4^{2-}, CrO_4^{2-}, MoO_4^{2-}, PO_4^{3-}, AsO_4^{3-}, etc. It is based upon tubules parallel to the *a* axis that consist of corner-sharing $\{UO_7^{8-}\}$ pentagonal bipyramids and $\{SeO_4^{2-}\}$ tetrahedra (Figure 2). Each $\{UO_7^{8-}\}$ pentagonal bipyramid shares its five equatorial corners with adjacent $\{SeO_4^{2-}\}$ tetrahedra, whereas each $\{SeO_4^{2-}\}$ tetrahedron is linked to three adjacent uranyl bipyramids. The composition of the tubule is $[(UO_2)_3(SeO_4)_5]^{4-}$, with a U/Se ratio of 3:5. The interiors of the tubules are occupied by K^+ ions and H_2O molecules, and there are additional K^+ ions and H_2O molecules, as well as NO_3^- groups, between the tubules. Within the $\{UO_7^{8-}\}$ bipyramids, the U–O bonds corresponding to the uranyl cations are in the range of 1.75–1.77 Å, whereas 2.36 to 2.45 Å are observed for the equatorial U–O bonds. The mean Se–O bond lengths within the $\{SeO_4^{2-}\}$ tetrahedra are in the range of 1.625–1.624 Å. The bond-valence sums for the U^{6+} and Se^{6+} positions[9] are in the range of 5.75–6.24 valence units. The $\{UO_7^{8-}\}$ bipyramids are distorted, with a nonplanar arrangement of the equatorial U–O bonds that is undoubtedly a consequence of the tubular character of the uranyl selenate unit.

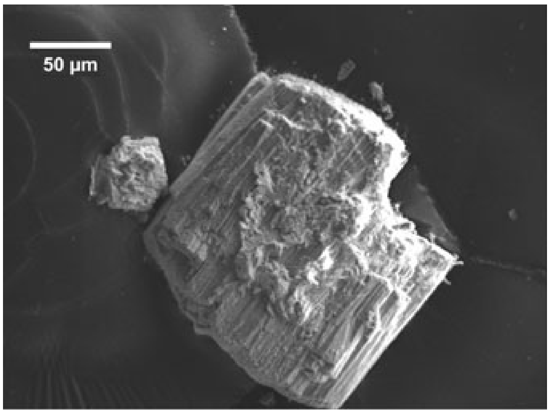

Figure 1. SEM image of a crystal of **1**.

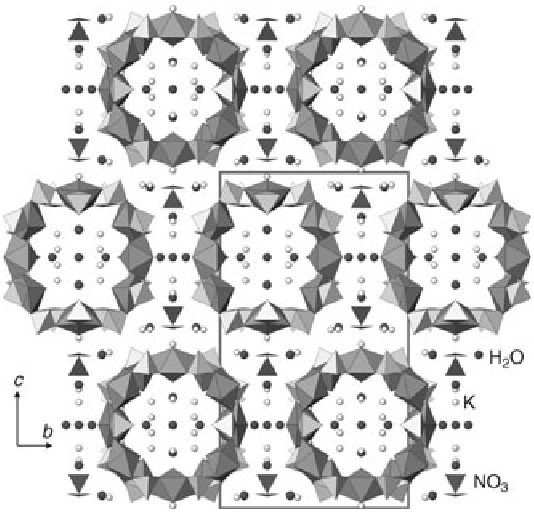

Figure 2. Crystal structure of **1** projected along the *a* axis. $\{UO_7^{8-}\}$ bipyramids are dark grey, $\{SeO_4^{2-}\}$ tetrahedra are light grey.

The size of the uranyl selenate $[(UO_2)_3(SeO_4)_5]^{4-}$ tubules in the structure of **1** is on the nanoscale. The external diameter

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[**] This work was financially supported by the Austrian Science Fund (FWF) (project M771-N10). We thank Prof. Dr. Ulrich Griesser for his help with the IR measurements.

DOI: 10.1002/ange.200462356

of the tubule is 17 Å (1.7 nm), whereas its internal diameter, measured as the distance between the closest oxygen atoms across the cavity, is 7.4 Å (0.74 nm). The latter value provides a crystallographic free-diameter of 4.7 Å, which is similar to those of the the small-pore zeolites[12] and other molecular sieves such as titanosilicate ETS-4.[13]

The topology of the $[(UO_2)_3(SeO_4)_5]^{4-}$ nanoscale tubules found in the structure of **1** can be described by means of a nodal representation that is especially suitable for the description of structures based upon coordination polyhedra of two types.[14] In this approach, the $\{UO_7^{8-}\}$ bipyramids and $\{SeO_4^{2-}\}$ tetrahedra are symbolized by black and white vertices, respectively, and the vertices 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 $[(UO_2)_3(SeO_4)_5]^{4-}$ tubule is shown in Figure 3a; its idealized, unfolded version is given in Figure 3b. To obtain the tubular graph corresponding to the $[(UO_2)_3(SeO_4)_5]^{4-}$ tubule (Figure 3a, c), one has to cut the graph into tapes along the lines indicated in Figure 3b, fold the tape, and glue its sides accordingly.

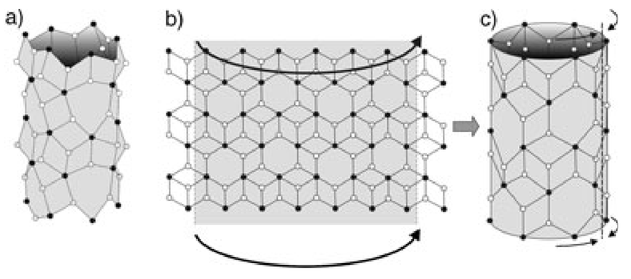

Figure 3. Nodal representation of the uranyl selenate tubule in the structure of **1** (a), its prototype 2D graph (b), and its idealized folded version (c). $\{UO_7^{8-}\}$ bipyramids and $\{SeO_4^{2-}\}$ tetrahedra are symbolized by black and white vertices, respectively.

Most of the inorganic nanotubes known have a prototype layered material from which they can be (at least theoretically) obtained by exfoliation of single-layer sheets and their folding up into a tube. The same holds for the uranyl selenate nanoscale tubules observed in the structure of **1**. The 3:5 black-and-white graph shown in Figure 3b is an underlying topology for a number of $[(UO_2)_3(TO_4)_5]^{4-}$ sheets found in the structures of inorganic oxo salts where T is S,[15] Cr,[16] or Se.[17] However, to define the topology of a sheet by means of its nodal representation is not enough to define its complete topological structure.[16,17] The point is that each $\{TO_4^{2-}\}$ tetrahedron in the sheet is three-connected, that is, it shares three of its four corners with adjacent $\{UO_7^{8-}\}$ bipyramids, thus leaving the fourth corner unshared. This gives rise to four classes of geometrical isomers of the $[(UO_2)_3(TO_4)_5]^{4-}$ sheets that differ in the orientation sequences of the tetrahedra (see ref. [16] for more details). Interestingly, none of the geometrical isomers observed in the layered phases corresponds directly to tetrahedra orientation of the uranyl selenate tubule observed in **1**. Exactly four of the five tetrahedra forming the tubule have their unshared corners oriented outside relative to the wall, whereas only one is oriented inside. This specificity of the topological structure of the tubule is a consequence of its cylindrical topology.

To be able to fold up into a tube, uranyl selenate units must possess geometrical flexibility. It has been shown[18] that the structural units observed in the structures of uranyl compounds with tetrahedral TO_4^{2-} oxoanions (T = S, Cr, Se, Mo) are very flexible. This results in a variety of topologically different structures[14] and a number of reconstructive[19] and displacive[20] phase transitions. It is therefore not surprising that the U-O-T links are flexible enough to permit folding of a layered fragment into a tubule.

We note that the $[(UO_2)_3(SeO_4)_5]^{4-}$ tubules observed in the structure of **1** cannot be referred to as nanotubes as this term is reserved for materials with the corresponding morphology,[2c] that is, for free-standing, nanoscale tubular objects. However, all known examples of tubular objects found in inorganic systems have their counterparts in the world of nanotubes (e.g. vanadium oxide nanotubes,[3,21] molybdenum sulfide nanotubes,[22] etc.). It should be mentioned that single crystals composed of highly ordered arrays of single-walled carbon nanotubes have also been obtained.[23] Remškar[2f] has reported that nanotubes with diameters less than a few tenths of a micrometer show a strong tendency to self-assemble, that is, to form ordered, crystalline structures that can be observed by X-ray diffraction techniques. These observations indicate that the fabrication of free-standing uranium oxidic nanotubes is highly likely under the appropriate conditions. This opens up a new area of research on uranium and actinide nanomaterials with possible applications in nanotechnology. In particular, this may lead to new solutions for the problem of utilization of depleted uranium, hundreds of thousands of tons of which is now stored by nuclear powers such as the U.S. and Russia.

In conclusion, we have succeeded in preparing a new inorganic material with a structure based upon nanoscale uranyl selenate tubules. It is the first example of a nanotubular structure observed for uranium compounds and the first example of an ordered nanotubular object observed in the structures of inorganic oxo salts.

Received: October 19, 2004

Keywords: nanotubes · oxides · selenium · solid-state structures · uranium

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[10] **1**: K_2CO_3 (0.045 g, 0.33 mmol), 40% H_2SeO_4 (0.15 mL, 1.46 mmol), and $(UO_2)(NO_3)_2\cdot 6H_2O$ (0.17 g, 0.34 mmol) were dissolved in 2 mL of distilled H_2O and stirred until the mixture was completely homogeneous. The solution was then poured into a watch glass and was kept at 60°C for about 30 min. An additional 0.2 mL of H_2O was then added and the solution was left to evaporate in a fumehood. Greenish-yellow crystals of **1** were formed in 10% yield within about 24 h. The compound was characterized by semiquantitative electron microprobe analysis. IR and Raman spectra were recorded and the presence of uranyl ions, selenate, and nitrate groups was confirmed.

[11] Crystallographic data for **1**: $K_5[(UO_2)_3(SeO_4)_5](NO_3)(H_2O)_{3.5}$: $M_r = 1845.42\ \mathrm{g\,mol^{-1}}$, plate-like crystal, $0.05 \times 0.06 \times 0.02\ \mathrm{mm^3}$, orthorhombic, *Pnmm*, $a = 11.2048(10)$, $b = 18.2132(19)$, $c = 32.364(3)$ Å, $V = 6604.7(11)$ Å^3, $Z = 8$, $\rho_{calc} = 3.712\ \mathrm{g\,cm^{-3}}$, $2\theta_{max} = 49.80°$, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, ω-scan (1° per image) at $\phi = 0°$ (STOE IPDS II), 293 K, 32004 measured reflections, 5875 independent reflections, 4657 reflections with $|F_o| \geq 4\sigma_F$ ($R_{int} = 0.120$, $R_\sigma = 0.063$), 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 (G. M. Sheldrick, program for the refinement of crystal structures, Göttingen, **1997**)), $R_1 = 0.080$, $wR_2 = 0.168$ for observed reflections, $R_1 = 0.103$, $wR_2 = 0.177$ for all data, max./min. electron density: 4.406/−1.982. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-414481.

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