DOI: 10.1002/anie.201004797

Elliptical Nanotubules

Differential Ion Exchange in Elliptical Uranyl Diphosphonate Nanotubules**

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Uranyl materials with nanotubular structures are a very small subset of the thousands of uranyl compounds that have been prepared, with only a handful of examples being known to date.[1–5] The first of these that was discovered is a uranyl phenylphosphonate (γ-UPP) in which the phenyl groups create the hydrophobic exterior of the nanotubules. This compound results from the room-temperature transformation of one-dimensional uranyl phenylphosphonates upon exposure to Na^+ or Ca^{2+} cations in an aqueous media.[1] Three other examples are uranyl selenates prepared by the slow evaporation of uranyl selenate solutions in the presence of organic templates or alkali metal cations.[2–5] Furthermore, an uranyl formate adopts nanotubulular structure.[6] Some of these nanotubules are anionic with cations in the interior of the nanotubules as well as in the space between the nanotubules. Very little is known about whether compounds in this class only represent interesting structures, or whether atypical properties can be derived from their unusual architectures.

We have recently demonstrated that 1,4-phenyldiphosphonate can be used in conjunction with uranyl cations and fluoride to create pillared structures. The voids between pillars and layers in these structures are filled with organic templates, and the templates significantly affect the type of structure adopted.[7] As an expansion of this work, we have probed how alkali metal and transition metal cations affect the structure of the uranyl diphosphonates. When Cs^+ cations are used to template the structure, a remarkable compound results: $Cs_{3.62}H_{0.38}[(UO_2)_4\{C_6H_4(PO_2OH)_2\}_3\{C_6H_4(PO_3)_2\}F_2]$ (**1**).

The structure of **1**, although nanotubular, is distinct from the previous members of this family in that it is highly elliptical, with tube dimensions of approximately 1×2 nm (Figure 1). The structure is composed of corner-sharing dimers of UO_7 pentagonal bipyramids that contain the uranyl cations. The shared atom is a fluoride anion, and therefore the inclusion of HF in the synthesis of **1** is essential. The remaining four sites in the equatorial plane of the uranyl cations are oxygen atoms from the diphosphonate ligand.

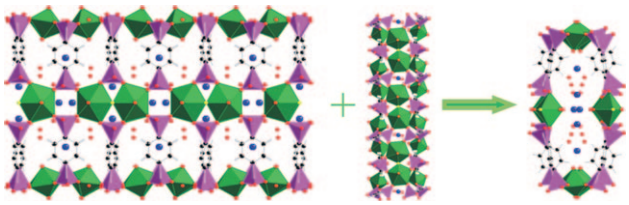

Figure 1. Three different views of the uranyl diphosphonate nanotubules in $Cs_{3.62}H_{0.38}[(UO_2)_4\{C_6H_4(PO_2OH)_2\}_3\{C_6H_4(PO_3)_2\}F_2]$ (**1**). UO_7 pentagonal bipyramids are shown in green, phosphonate tetrahedra in violet; O red, F yellow, Cs blue.

The PO_3 moieties play a number of interesting roles in the structure. First, they span between the uranyl cations to help create the dimers. They also bridge between the dimers to create one-dimensional chains that extend along the length of the nanotubules. Two such chains exist in the structure: one along the short side of the nanotubules (11.7 Å), and second along the long side (21.0 Å). These chains have nearly identical topologies and differ only in that the former are slightly canted, and the latter are not. This one-dimensional topology has been observed in uranyl molybdates.[8] The reason for the differences in dimensions of the sides of the nanotubules is that the phenyl rings expand two parallel sides of the ellipses.

The nanotubules are anionic. Some of the charge is compensated by protonating terminal P–O groups as indicated by the formula. The protonation of the phosphonate moieties is nonstoichiometric, leading to partial occupancy of some of the Cs^+ cations that located both within the nanotubules and between the nanotubules (Figure 2).

The key feature that this nanotubular structure creates is different chemical environments for the Cs^+ cations within and outside of the tubes. The Cs^+ cations within the tubes are bound by water molecules, fluoride ions, oxo atoms from the uranyl cations, bridging phosphonate oxygen atoms, and by π interactions with the phenyl rings of the phosphonate ligands (Figure 3). The Cs^+ cations located on the outside of the tubes are bound by water molecules, the uranyl oxo atoms, and by the oxygen atoms from the phosphonate ligands that are not involved in bonding with uranium. The $Cs^+\cdots O$ interactions vary considerably from 2.79(3) to 3.680(7) Å. It appears that the latter cations are most likely held by stronger interactions than those within the tubes, and we therefore

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[**] We are grateful for support provided by the Chemical Sciences, Geosciences, and Biosciences Division, the Office of Basic Energy Sciences, the Office of Science, and the Heavy Elements Program, U.S. Department of Energy, under Grant DE-FG02-01ER16026. This material is based upon work supported as part of the Materials Science of Actinides, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001089.

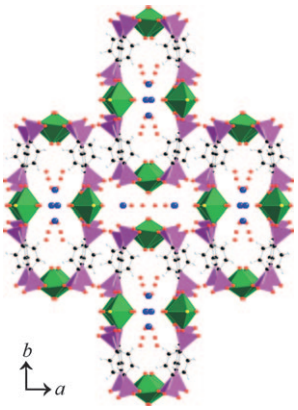

Figure 2. A view down the *c* axis of **1**, showing the packing of the uranyl phosphonate nanotubules that creates channels that house additional Cs^+ cations. UO_7 pentagonal bipyramids are shown in green, phosphonate tetrahedra in violet; C black, O red, F yellow, Cs blue.

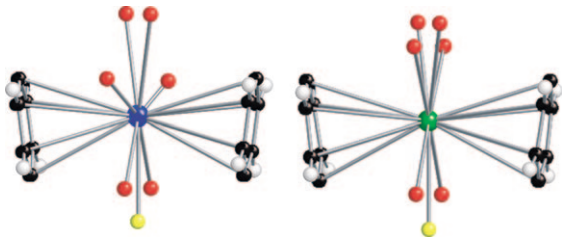

Figure 3. Environment of one of the Cs^+ cations (in **1**) and Ag^+ cations (in **2**) within the nanotubules (after ion exchange), showing the interactions with the phenyl rings of the diphosphonate ligands. C black, O red, Cs blue, Ag green, F yellow, H white.

tested this proposal using cation-exchange experiments. In particular, the use of Ag^+ as the cation exchanger might allow much stronger interactions with the phenyl rings within the tubes.

The immersion of the crystals of **1** in solutions of silver nitrate for 7 days resulted in cation exchange without destruction of the crystals; the single crystals remain intact and can be re-investigated using single-crystal X-ray diffraction after ion exchange. These diffraction experiments revealed that the Cs^+ cations within the tubes were completely replaced by Ag^+, whereas only partial exchange with the Cs^+ cations within the channels between the nanotubules occurred, yielding a final Ag/Cs ratio in $Ag_{2.46}Cs_{1.54}[(UO_2)_4\{C_6H_4(PO_2OH)_2\}_3\{C_6H_4(PO_3)_2\}F_2]\cdot nH_2O$ (**2**) of 1.59:1. These results were bolstered by SEM-EDAX measurements, which confirm the presence of both Cs^+ and Ag^+ within the crystals of **2** in ratios (1.56:1) that are similar to that found from the single-crystal data. However, the interactions with the phenyl rings are not the driving force for the exchange as originally predicted, but rather new short contacts between the Ag^+ cations and the uranyl oxo atoms exist in the exchanged material, creating a square-planar environment around the Ag^+ cations near the center of the nanotubules, with Ag–O bond distances of 2.509(16) Å (twice) and 2.569(18) Å (twice). The U=O bond lengths that are involved in these interactions are largely unaltered upon formation of these interactions, and are still within normal limits. Owing to the large range of the $Cs^+\cdots O$ interactions it is difficult to discern if these are altered by the ion exchange. These results demonstrate two different phenomena. First, the nanotubules are rigid and are unaltered by ion exchange. Second, the chemical environment within the interior of the nanotubules is different from that of the interior channels between the nanotubules.

A testament to the stability and rigidity of the nanotubules versus alternative frameworks comes from comparative studies with uranyl diphosphonates lacking nanotubular structures. For example, when the pillared compound $[C_{12}H_{10}N_2][(UO_2)_3\{C_6H_4(PO_3)_2\}_2]\cdot H_2O$ (**3**) is subjected to cation exchange or immersion in water, the structure undergoes a substantial rearrangement and recrystallization: from a three-dimensional network in which the diphosphonate ligand bridges between layers to a layered structure in which the diphosphonate bridges between one-dimensional chains in $[C_{12}H_{10}N_2][UO_2\{C_6H_4(PO_3)_2\}]$, that is, the inverse of the rearrangement of the structure of one-dimensional α- and β-UPP to nanotubular γ-UPP[1] (Figure 4). The new compound contains edge-sharing dimers of UO_7 pentagonal bipyramids that are bridged by the PO_3 moieties of the diphosphonate to create one-dimensional chains. It is interesting to note that U–O bonds with phosphate and phosphonates are strong, and yet they are clearly labile in some systems. Uranyl phosphates are solubility-limited phases in some natural environments. We clearly have not yet reached the point where we can predict structural stability based solely on the bonding and architecture.

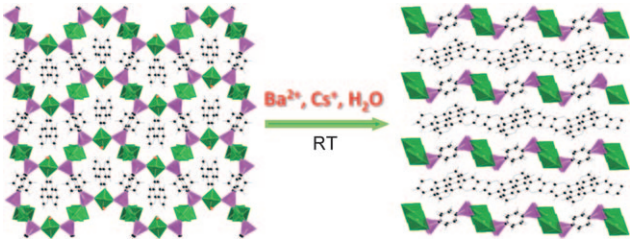

Figure 4. Rearrangement of the structure of $[C_{12}H_{10}N_2][(UO_2)_3\{C_6H_4(PO_3)_2\}_2]\cdot H_2O$ (**3**) from a pillared structure to a layered structure upon exposure to various cations in aqueous media.

This work has yielded several important observations and conclusions. First, uranyl nanotubules can be derived in high yield from complex and large oxoanions, such as 1,4-phenyldiphosphonate. All previous examples utilized smaller anions. The large linker between the uranyl cations yields elliptical nanotubules instead of ones with nearly circular cross-sections. Second, these nanotubules are robust, and the single crystals withstand ion exchange without degradation of their crystallinity. Third, compounds of similar composition, but different architectures (for example pillared structures) respond differently to ion exchange and simple immersion in water than does the related nanotubular material. We therefore conclude that uranyl nanotubules

are not simply interesting structures but rather physicochemical property relationships can be derived from the differences of the chemical environments within the nanotubules versus the environments around them.

Experimental Section

$UO_2(C_2H_3O_2)_2{\cdot}2H_2O$ (42.5 mg, 0.1 mmol), 1,4-benzenebisphosphonic acid (47.7 mg, 0.2 mmol), CsCl (16.9 mg, 0.1 mmol), Millipore water (0.7 mL), and two drops of 48% HF were loaded into a 23 mL autoclave. The autoclave was sealed and heated to 200°C in a box furnace for 3 days. The autoclave was then cooled at an average rate of 5°C hr^{-1} to 25°C. The resulting yellow product was washed with boiling water to remove excess phosphonic acid, followed by rinsing with methanol, and allowed to dry in air at room temperature. Yellow tablets of **1** as a pure phase suitable for X-ray diffraction studies were formed. The synthesis can also be carried out by using uranyl nitrate as the source of uranium. Single-crystal X-ray diffraction and powder X-ray diffraction studies reveal that **1** forms as a pure phase with a yield of 70.5% based on U.

$Cs_{3.62}H_{0.38}[(UO_2)_4\{C_6H_4(PO_2OH)_2\}_3\{C_6H_4(PO_3)_2\}F_2]$ (**1**): yellow tablets, crystal dimensions $0.045\times0.040\times0.028$ mm^3, monoclinic, $C2/m$ (No. 12), $Z=8$, $a=21.550(2)$, $b=23.951(2)$, $c=10.3896(9)$ Å, $\beta=99.490(2)°$, $V=5289.1(8)$ Å^3 ($T=100$ K), $\mu=150.1$ cm^{-1}, $R_1=0.0388$, $wR2=0.0842$. Bruker APEXII Quazar diffractometer: $\theta_{max}=52.70°$, MoKα, $\lambda=0.71073$ Å, 0.5° ω scans, 29084 reflections measured, 5521 independent reflections, all of which were included in the refinement. The data was corrected for Lorentz polarization effects and for absorption; the structure was solved by direct methods, anisotropic refinement of F^2 by full-matrix least-squares, 345 parameters.[9] $Ag_{2.46}Cs_{1.54}[(UO_2)_4\{C_6H_4(PO_2OH)_2\}_3\{C_6H_4(PO_3)_2\}F_2]{\cdot}nH_2O$ (**2**) (Z is doubled for this formula): yellow tablets, crystal dimensions $0.044\times0.039\times0.028$ mm^3, monoclinic, $C2/m$ (No. 12), $Z=8$, $a=21.555(2)$, $b=23.937(1)$, $c=10.3787(6)$ Å, $\beta=99.838(4)°$, $V=5276.3(6)$ Å^3 ($T=100$ K), $\mu=145.12$ cm^{-1}, $R_1=0.0464$, $wR2=0.1165$. Bruker APEXII Quazar diffractometer: $\theta_{max}=47.90°$, MoKα, $\lambda=0.71073$ Å, 0.5° ω scans, 14346 reflections measured, 4221 independent reflections, all of which were included in the refinement. The data was corrected for Lorentz polarization effects and for absorption; the structure was solved by direct methods, anisotropic refinement of F^2 by full-matrix least-squares, 335 parameters.[9] $[C_{12}H_{10}N_2][(UO_2)_3\{C_6H_4(PO_3)_2\}_2]$ (**3**): yellow tablets, crystal dimensions $0.100\times0.063\times0.030$ mm^3, triclinic, $P\bar{1}$, (No. 2), $Z=2$, $a=9.5417(3)$, $b=9.9607(3)$, $c=10.9998(3)$ Å, $\alpha=87.85$, $\beta=66.54$, $\gamma=87.98°$, $V=958.14(5)$ Å^3 ($T=100$ K), $\mu=86.91$ cm^{-1}, $R_1=0.0165$, $wR2=0.0413$. Bruker APEXII Quazar diffractometer: $\theta_{max}=56.58°$, MoKα, $\lambda=0.71073$ Å, 0.5° ω scans, 11591 reflections measured, 4551 independent reflections, all of which were included in the refinement. The data was corrected for Lorentz polarization effects and for absorption; the structure was solved by direct methods, anisotropic refinement of F^2 by full-matrix least-squares, 280 parameters.[9] CCDC 485459 (**1**), CCDC 485460 (**2**), and CCDC 485466 (**3**) 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.

Received: August 2, 2010
Published online: October 12, 2010

Keywords: ion exchange · nanotubules · phosphonates · structural transformation · uranium

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