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Uranium(VI) Tetraoxido Core Coordinated by Bidentate Nitrate

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The synthesis and structural characterization of the compounds $K[(UO_2)_2(UO_4)(OH)(NO_3)_2]H_2O$ (**1**) and $Ba[(UO_2)_4(UO_4)_2(OH)_2(NO_3)_4]H_2O$ (**2**) have revealed that each contains sheets that are based upon the β-U_3O_8-type topology and that these sheets are linked through low-valence interlayer cations. Consistent with other uranium(VI) compounds that have topologically identical sheets, one of the uranium(VI) sites exhibits a highly unusual $(UO_4)^{2-}$ tetraoxido core that is further coordinated by two bidentate $(NO_3)^-$ groups.

The crystal and coordination chemistry of uranium(VI) is heavily dominated by the linear $(UO_2)^{2+}$ uranyl ion.[1−3] This uranyl ion almost always occurs coordinated by four, five, or six ligands arranged at the equatorial vertices of square, pentagonal, or hexagonal bipyramids, respectively. The apical ligands of the bipyramids correspond to the O atoms of the uranyl ion, and linkages within the structural units are seldom through these sites. Uranyl polyhedra in inorganic compounds link into structural units through their equatorial vertices, most commonly resulting in infinite sheets, although chains and frameworks are also important.[1] Several recent studies have challenged our understanding of the normally unreactive uranyl ion,[4−10] and recently uranium(VI) has been reported to adopt a tetraoxido core rather than the uranyl ion.[11] We are particularly interested in the role of structural features that stabilize uncommon actinide polyhedra such as the tetraoxido core.

We have previously examined the topological aspects of sheets of uranyl polyhedra in minerals and synthetic inorganic materials.[1,12] There is a myriad of complex structural sheets, some of which contain only uranyl bipyramids and others that contain various oxyanions that bridge between the uranyl bipyramids. One of the most interesting topologies was first found in mixed-valence β-U_3O_8.[13] This β-U_3O_8 topology consists of chains of edge-sharing pentagonal bipyramids that are one polyhedron wide. These are linked into a sheet by the sharing of vertices between every second bipyramid of adjacent chains (Figure 1). There are spaces between these chains of bipyramids that are incompatible with uranyl pentagonal or hexagonal bipyramids because of geometric restrictions created by the proximity of only four potential equatorial vertices. In several compounds, these square sites are occupied by U cations with unusual coordination polyhedra. In the calcium uranyl carbonate minerals wyartite and dehydrated wyartite, the square sites are occupied by seven-coordinated uranium(V), with the coordination polyhedra completed by an H_2O group on one side and a bidentate $(CO_3)^{2-}$ triangle on the other side.[14,15] Square sites in the same sheet topology in $[U^{V}(H_2O)_2(U^{VI}O_2)_2O_4(OH)](H_2O)_4$ contain uranium(V) that has four short equatorial bonds to O atoms at 2.059 Å and two longer apical O atoms at 2.410 and 2.438 Å.[16] Spriggite, a lead uranyl hydroxide mineral, contains topologically identical sheets with the square sites occupied by uranium(VI) in a highly distorted octahedral coordination with four bond lengths between 1.84(4) and 2.07(4) Å and two longer bonds to ligands at 2.28(3) and 2.33(3) Å.[17] A total of 50% of the square sites in sheets in the compound $Cd_2(H_2O)_2[U(OH)(CH_3COO)(UO_2)_5(OH)_2O_8]\cdot 0.5H_2O$ contain uranium(VI) with a tetraoxido core, with four short equatorial bonds ranging from 1.961(7) to 2.000(7) Å and two apical O atoms at distances of 2.306(8) and 2.340(7) Å.[11] U^{VI} cations with similar tetraoxido-like cores occur in square sites in the analogous

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(1) Burns, P. C. *Can. Mineral.* **2005**, *43*, 1839–1894.

(2) Burns, P. C.; Ewing, R. C.; Hawthorne, F. C. *Can. Mineral.* **1997**, *35*, 1551–1570.

(3) Morss, L. R.; Edelstein, N. M.; Fuger, J.; Katz, J. J. *The chemistry of the actinide and transactinide elements*; Springer: Dordrecht, The Netherlands, 2006; p 3440.

(4) Arnold, P. L.; Patel, D.; Wilson, C.; Love, J. B. *Nature* **2008**, *451*, 315–U3.

(5) Boncella, J. M. *Nature* **2008**, *451*, 250–252.

(6) Burns, C. J. *Science* **2005**, *309*, 1823–1824.

(7) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. *Science* **2005**, *309*, 1835–1838.

(8) Fox, A. R.; Bart, S. C.; Meyer, K.; Cummins, C. C. *Nature* **2008**, *455*, 341–349.

(9) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Palmer, P. D.; Batista, E. R.; Hay, P. J. *Science* **2005**, *310*, 1941–1943.

(10) Summerscales, O. T.; Cloke, F. G. N.; Hitchcock, P. B.; Green, J. C.; Hazari, N. *Science* **2006**, *311*, 829–831.

(11) Wu, S. J.; Ling, J.; Wang, S. A.; Skanthakumar, S.; Soderholm, L.; Albrecht-Schmitt, T. E.; Alekseev, E. V.; Krivovichev, S. V.; Depmeier, W. *Eur. J. Inorg. Chem.* **2009**, 4039–4042.

(12) Burns, P. C.; Miller, M. L.; Ewing, R. C. *Can. Mineral.* **1996**, *34*, 845–880.

(13) Loopstra, B. O. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1970**, *B26*, 656–657.

(14) Hawthorne, F. C.; Finch, R. J.; Ewing, R. C. *Can. Mineral.* **2006**, *44*, 1379–1385.

(15) Burns, P. C.; Finch, R. J. *Am. Mineral.* **1999**, *84*, 1456–1460.

(16) Belai, N.; Frisch, M.; Ilton, E. S.; Ravel, B.; Cahill, C. L. *Inorg. Chem.* **2008**, *47*, 10135–10140.

(17) Brugger, J.; Krivovichev, S. V.; Berlepsch, P.; Meisser, N.; Ansermet, S.; Armbruster, T. *Am. Mineral.* **2004**, *89*, 339–347.

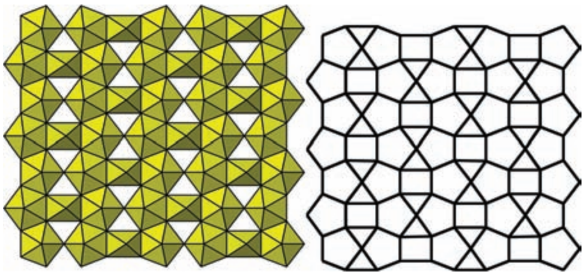

Figure 1. Polyhedral representation of the classic β-U_3O_8-type sheet and its corresponding sheet anion topology.[12].

sheets in $(NH_4)_3(H_2O)_2[(UO_2)_{10}O_{10}(OH)][(UO_4)(H_2O)_2]$ and $Sr_5(UO_2)_{20}(UO_6)_2O_{16}(OH)_6(H_2O)_6$.[18,19] Thus, it is apparent that uranium compounds with sheets of the β-U_3O_8 topology are fertile areas for the study of unusual uranium coordination polyhedra. In the course of hydrothermal synthesis experiments in the aqueous uranyl chromate system, we obtained two isotypic compounds containing sheets with the β-U_3O_8 topology that exhibit yet another remarkable uranium(VI) coordination environment.

Crystals of the compounds $K[(UO_2)_2(UO_4)(OH)(NO_3)_2]H_2O$ (**1**) and $Ba[(UO_2)_4(UO_4)_2(OH)_2(NO_3)_4]H_2O$ (**2**) were obtained from hydrothermal experiments conducted at 220 °C.[20] Single-crystal X-ray diffraction data were used to solve and refine the structures of these compounds.[21]

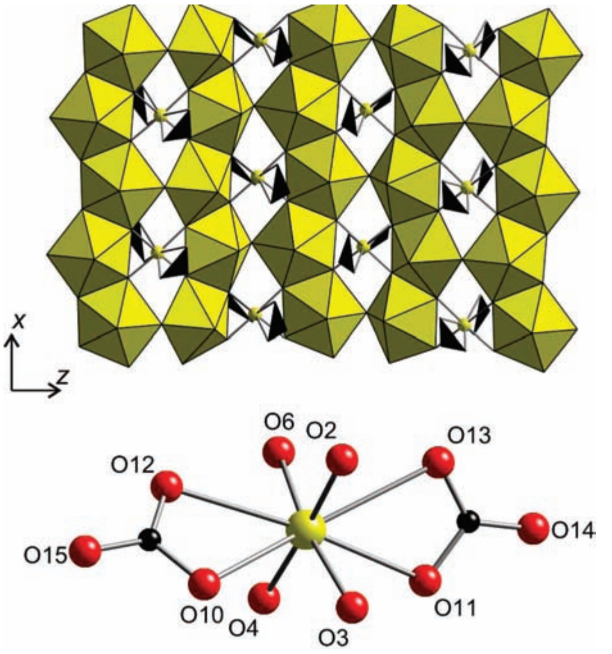

Figure 2. Sheet of uranium(VI) polyhedra in the structures of **1** and **2** (top). The U2 and U3 pentagonal bipyramids are shown in yellow. The U1 cation is represented by yellow spheres, and the $(NO_3)^-$ groups are shown as black triangles. On the bottom are the details of the U1 coordination geometry.

Both compounds under study contain sheets with the β-U_3O_8 topology (Figure 2). Each such sheet contains three uranium(VI) sites. The U2 and U3 cations are present as normal $(UO_2)^{2+}$ uranyl ions with bond lengths in the range of 1.755(12)−1.788(8) Å, which are typical.[2] These uranyl ions are further coordinated by five O atoms arranged in the equatorial plane of pentagonal bipyramids with bond lengths in the range of 2.263(10)−2.484(12) Å. These are the uranyl pentagonal bipyramids that form chains by the sharing of equatorial edges and the extended sheet by the sharing of vertices between adjacent chains.

The U1 cation is located within the square sites of the β-U_3O_8 sheet topology. It is bonded to four approximately coplanar O atoms that are equatorial vertices of pentagonal bipyramids in the adjacent chains. In compound **1**, the corresponding bond lengths range from 1.971(8) to 2.040(8) Å and, in compound **2**, from 1.969(12) to 2.034(10) Å. Note that these bond lengths are very similar to those found in $Cd_2(H_2O)_2[U(OH)(CH_3COO)(UO_2)_5(OH)_2O_8]\cdot 0.5H_2O$, which are designated as a tetraoxido core. Unlike in this latter compound, where the uranium(VI) is coordinated by two additional O atoms with bond distances of ~2.3 Å, the U1 sites in compounds **1** and **2** are coordinated by two bidentate $(NO_3)^-$ groups located on opposite sides of the sheets. In **1**, the corresponding U−O bond lengths are 2.509(10), 2.533(11), 2.567(10), and 2.711(14) Å, and in **2**, they are 2.492(12), 2.565(14), 2.583(14), and 2.702(16) Å. These are the first examples of a uranium(VI) tetraoxido core coordinated by two bidentate $(NO_3)^-$ groups. The $(NO_3)^-$ groups, which have been confirmed by IR spectroscopy, have average N−O bond lengths of 1.24 and 1.23 Å for **1** and **2**, respectively. The displacement parameters of the O atoms of the $(NO_3)^-$ groups are elongated and are larger than those of the other O atoms in the structure, suggesting some degree of disorder. Bond-valence-sum calculations using coordination-nonspecific parameters[2] give 5.88 vu (valence units) for the U1 sites in both

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(18) Kubatko, K. A.; Burns, P. C. *Inorg. Chem.* **2006**, *45*, 10277–10281.

(19) Li, Y. P.; Cahill, C. L.; Burns, P. C. *Chem. Mater.* **2001**, *13*, 4026–4031.

(20) ***Caution!*** *Chromium(VI) compounds are carcinogenic, so extra care is required in their handling. All uranium samples in the following experiments were isotopically depleted; however, standard safety precautions for working with radioactive materials should still be followed.* $Ba(NO_3)_2$ (99+%, Alfa Aesar), CrO_3 (99.8%, Baker Analyzed), $K(NO_3)$ (99+%, Aldrich), LiOH (98%, Alfa Aesar), HNO_3 (70%, Fisher), and $UO_2(NO_3)_2\cdot 6H_2O$ (International Bio-Analytical Int.) were used as received. Millipore-filtered ultrapure water (18 MΩ resistance) was used in all reactions. Yellow-brown blade crystals of $K[(UO_2)_2(UO_4)(OH)(NO_3)_2]H_2O$ (**1**) were crystallized by the hydrothermal reaction of 2.5 mL of 0.2 M aqueous uranyl nitrate hexahydrate with 0.5 mL of 0.2 M aqueous CrO_3 and 0.5 mL of aqueous 0.2 M KNO_3. The pH was adjusted to 4 by the addition of 2 M aqueous LiOH. Yellow-brown blade crystals of $Ba[(UO_2)_4(UO_4)_2(OH)_2(NO_3)_4]H_2O$ (**2**) were crystallized by the hydrothermal reaction of 2.5 mL of 0.2 M aqueous uranyl nitrate hexahydrate with 0.5 mL of 0.2 M aqueous CrO_3 and 0.5 mL of 0.2 M aqueous $Ba(NO_3)_2$. The pH was adjusted to 4 by the addition of 2 M aqueous LiOH. These solutions were placed in Teflon-lined stainless steel reaction vessels that were heated at 220 °C for 7 days. Crystals were recovered by filtration and were washed with deionized water. The presence of multiple unidentified secondary phases precluded measurement of the yields. Multiple syntheses excluding CrO_3 were unsuccessful in producing compound **1** or **2**, although the role of chromate in the hydrothermal reactions is unknown.

(21) Crystals were mounted on a Bruker PLATFORM three-circle X-ray diffractometer equipped with a 4K APEX CCD detector and graphite-monochromatized Mo Kα radiation with a crystal-to-detector distance of 6.0 cm. A sphere of data was collected using framewidths of 0.5° in ω at room temperature. Intensity data were corrected for Lorentz, polarization, and background effects using the Bruker program APEX II. A semiempirical correction for adsorption was applied in each case using the program *SADABS*. The *SHELXTL*, version 5, series of programs was used for the solution and refinement of the crystal structures. Evaluation of the data for **1** revealed nonmerohedral twinning consisting of two components related by a 179.9° rotation that was subsequently addressed by the refinement procedure. Tentative H atom positions were located and refined with the soft constraint that donor O−H bonds be ~0.96 Å. Compound **1**: yellow-brown bladelike crystals, orthorhombic, *Pbca*, a = 7.2675(8) Å, b = 17.1197(20) Å, c = 21.5511(24) Å, V = 2681.3(5) Å^3, R1 = 6.00%, wR2 = 13.66%, S = 0.96, 2536 unique reflections. Compound **2**: yellow-brown bladelike crystals, orthorhombic, *Pbca*, a = 7.2616(13) Å, b = 17.0969(31) Å, c = 21.5497(39) Å, V = 2675.4(8) Å^3, R1 = 3.46%, wR2 = 9.07%, S = 1.04, 3330 unique reflections.

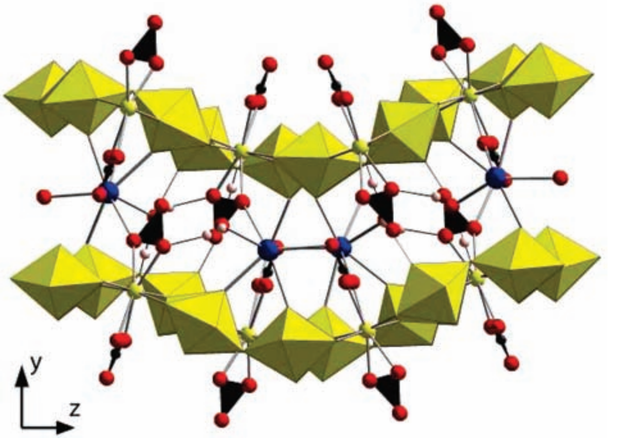

Figure 3. Projection of the structure of **2** showing the sheet corrugation and the connectivity between the sheets. U2 and U3 pentagonal bipyramids are shown in yellow. The U1 cation is shown as a yellow sphere, and $(NO_3)^-$ groups are shown as black triangles, Ba cations as blue spheres, O atoms as red spheres, and H atoms as small gray spheres.

compounds, consistent with the formal oxidation state. However, exclusion of the O atoms of the nitrate groups from the calculation results in only 4.42 and 4.43 vu for U1 in **1** and **2**, respectively. This result clearly indicates the importance of the bidentate $(NO_3)^-$ groups in completing the U1 coordination polyhedron. Just as coordinating ligands about the $(UO_2)^{2+}$ uranyl ion are needed in crystal structures, significant contributions to the bonding requirements of $(UO_4)^{2-}$ by coordinating ligands are also mandatory.

The sheets in compounds **1** and **2** are rather corrugated, possibly to enhance connectivity with the interlayer constituents (Figure 3). Adjacent sheets are linked through bonds to the K or Ba cations, as well as through a hydrogen-bonding network.

Computational studies of the $(UO_4)^{2-}$ tetraoxido core indicate that a tetrahedral arrangement of O atoms about the U^{VI} cation is favored over the approximately square-planar geometry that we have found in the current structures, as well as those in previously reported structures.[22] However, a tetrahedral geometry is incompatible with the β-U_3O_8 sheet topology, which apparently stabilizes the square-planar geometry.

Given the almost complete dominance of the $(UO_2)^{2+}$ uranyl ion in the crystal chemistry of uranium(VI), the role of the β-U_3O_8 sheet topology in stabilizing unusual uranium(VI) coordination geometries is rather remarkable. It is tempting to assume that such a sheet containing these unusual uranium(VI) polyhedra is unstable relative to alternative configurations, but the persistence of several compounds with these sheets (minerals) for geological times in highly complex geochemical environments indicates otherwise.

It is apparent that either unusual coordination geometries about uranium(VI) stabilize the β-U_3O_8 sheet topology or the topology itself stabilizes these uncommon uranium(VI) polyhedra. We tend to favor the latter scenario, although with hesitation. Almost 2 decades ago, Brown[23] explored the interplay between chemical and steric requirements in the crystal structures of inorganic compounds. He found that unlikely oxidation states and stoichiometries can be stabilized by the steric constraints of the extended structure. However, the well-known α-U_3O_8 sheet topology, which only contains uranyl pentagonal bipyramids and is known from several minerals and even more synthetic compounds, can be obtained from the β-U_3O_8 topology from relatively minor distortions. Uranium(VI) compounds containing sheets with the α-U_3O_8 and β-U_3O_8 topologies would be interesting subjects for the measurement of thermodynamic parameters to provide insight into the energetic penalty associated with nonuranyl uranium(VI) coordination geometries.

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Supporting Information Available: Crystallographic CIF file for **1** and **2**, crystallographic tables, and IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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[22] Bolvin, H.; Wahlgren, U.; Gropen, O.; Marsden, C. *J. Phys. Chem. A* **2001**, *105*, 10570–10576.

[23] Brown, I. D. *Acta Crystallogr. B* **1992**, *48*, 553–572.