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An Unprecedented Uranyl Phosphate Framework in the Structure of $[(UO_2)_3(PO_4)O(OH)(H_2O)_2](H_2O)$

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The new uranyl phosphate $[(UO_2)_3(PO_4)O(OH)(H_2O)_2]$ (H_2O) (**1**) with an unprecedented framework structure has been synthesized at 150 and 185 °C. The structure (tetragonal, $P4_2/mbc$, $a = 14.015(1)$ Å, $c = 13.083(2)$ Å, $V = 2575.6(4)$ Å^3, $Z = 8$) contains uranyl phosphate chains composed of uranyl pentagonal and hexagonal bipyramids and phosphate tetrahedra linked by sharing of polyhedral edges. The uranyl phosphate chains are aligned both along [100] and [010] and are linked into a novel framework structure involving channels along [001]. Topologically identical chains occur linked into sheets in more than a dozen uranyl phosphate minerals, but these chains have never been observed in opposing orientations and linked into a framework as in **1**.

Recent studies of uranyl minerals and compounds are largely motivated by their potential impact upon the mobility of radionuclides in a geological repository for nuclear waste and in vadose zones contaminated with actinides.[1] The crystal chemistry of uranyl minerals and compounds is richly diverse.[2] Polymerization of uranyl polyhedra, either with other uranyl polyhedra or other polyhedra of high bond valence, is common, although sheets of polyhedra tend to dominate due to the uneven distribution of bond strengths within uranyl polyhedra.[2] Less than 15% of known structures of inorganic uranyl phases involve frameworks of polyhedra of high bond valence,[2] although uranyl frameworks are of interest because of potential applications in areas such as separations, catalysis, and nuclear waste immobilization.[3] Frameworks containing only uranyl polyhedra have recently been discovered,[4] although each of these involve some U^{6+} in distorted octahedral coordination with no uranyl ion present. Linkages in the third dimension are also facilitated by non-uranyl polyhedra, such as silicates,[5] molybdates,[6] and vanadates.[7]

More than 40 uranyl phosphate minerals are known from nature[8] and are important for understanding the mobility of uranium in natural systems and in soils contaminated by actinides.[9] As part of our ongoing study of the crystal chemistry of uranyl phosphates,[10–12] we are exploring hydrothermal and gel-diffusion procedures for preparation of compounds with novel structural topologies.

Hydrothermal treatment of crystals of natural albite ($NaAlSi_3O_8$) with inclusions of a variety of natural phosphates with 0.1 M solution of $(UO_2)(NO_3)_2(H_2O)_6$ resulted in excellent crystals of $[(UO_2)_3(PO_4)O(OH)(H_2O)_2](H_2O)$ (**1**).[13] Electron microprobe analysis (standards: UO_2 and $Ca_2P_2O_7$; 15 kV, 25 nA) of five points gave 70.5 ($\sigma = 2.5$) and 2.4 ($\sigma = 0.5$) wt % for U and P, respectively, in

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(13) $[(UO_2)_3(PO_4)O(OH)(H_2O)_2](H_2O)$ (**1**) was obtained during the course of experiments designed to model the interaction of uranyl-bearing solutions with silicate minerals. It was obtained by treating natural albite ($NaAlSi_3O_8$) containing inclusions of phosphate minerals with 0.1 M $(UO_2)(NO_3)_2(H_2O)_6$ solution at pH 2.3 in Teflon-lined reaction vessels. Crystals of **1** were recovered following heating both at 150 and 185 °C for 7 days. In both cases, yields were low and amounted to a few dozen tabular crystals with dimensions approaching 100 μm.

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reasonable agreement with the expected values of 73.3 and 3.2 wt %. No other cations were detected. The infrared spectrum[14] of **1** confirmed the presence of H_2O and H bonds, and it contains five modes in the range 824−1096 cm^{-1} that are attributable to uranyl and phosphate vibrations.

The structure of **1**[15] contains three symmetrically independent U^{6+} cations, each of which is strongly bonded to two O atoms, giving $(UO_2)^{2+}$ uranyl ions (O_{Ur}). U1 and U2 involve linear uranyl ions that are coordinated by four O atoms and two OH groups in the case of U1, and six O atoms in the case of U2. The U3 uranyl ion is distorted to 176.3(3)° and is coordinated by three O atoms, one OH group, and one H_2O group. The $U-O_{Ur}$ bonds range from 1.755(7) to 1.772(8) Å, whereas the equatorial U−O bond lengths range from 2.240(7) to 2.608(6) Å, values that are typical of U^{6+} coordination polyhedra in well-refined structures.[2] The two phosphate tetrahedra have P−O bond lengths in the range 1.537(5)−1.539(5) Å. Bond-valence sums at the cation sites, calculated using parameters for U−O[2] and P−O,[16] are 5.98, 6.10, 6.17, 4.80, and 4.76 for U1, U2, U3, P1, and P2, respectively. The bond-valence sums at the O positions, excluding contributions from H bonds, range from 1.71 to 2.05 in the case of O and are 1.51 and 0.46 for the OH and H_2O groups, respectively.

The structure of **1** consists of an unprecedented uranyl phosphate framework composed of uranyl pentagonal and hexagonal bipyramids, as well as phosphate tetrahedra. Pairs of uranyl pentagonal bipyramids are connected by a common equatorial edge, with the resulting dimer linked to two hexagonal bipyramids; the linkage in each case involves two equatorial edges (Figure 1). Each uranyl hexagonal bipyramid is attached to two dimers of uranyl pentagonal bipyramids, resulting in a chain of polyhedra. The only equatorial vertex of a uranyl polyhedron that is not shared within the chain corresponds to the O9 position, which is occupied by H_2O. Phosphate tetrahedra are attached to both equatorial sides of the chain by sharing edges with the uranyl hexagonal bipyramids (Figure 1). The resulting uranyl phosphate chain is topologically identical to those that occur in the phosphuranylite group of minerals, although in these the chains are linked into sheets. Remarkably, the structure of **1** is a framework of interconnected uranyl phosphate chains that extend along [100] and [010], and each phosphate tetrahedron is linked to two chains by sharing two tetrahedral edges with uranyl hexagonal bipyramids of adjacent chains (Figure 2). The linkage of two edges of a phosphate tetrahedron with two uranyl polyhedra is a new mode of structural connectivity in uranyl phosphates and permits the formation of the novel framework of **1**. The structure also contains channels extending along [001] that contain H_2O (Figure 2). The channel width, measured between the center of the uranyl ion O atoms on either side, is 3.67 Å. As is typical for structures of uranyl compounds determined by X-ray diffraction, it was not possible to locate the H atoms. Consideration of anion−anion separations indicates H bonds extend between OH and H_2O bonded to U and O_{Ur} anions of

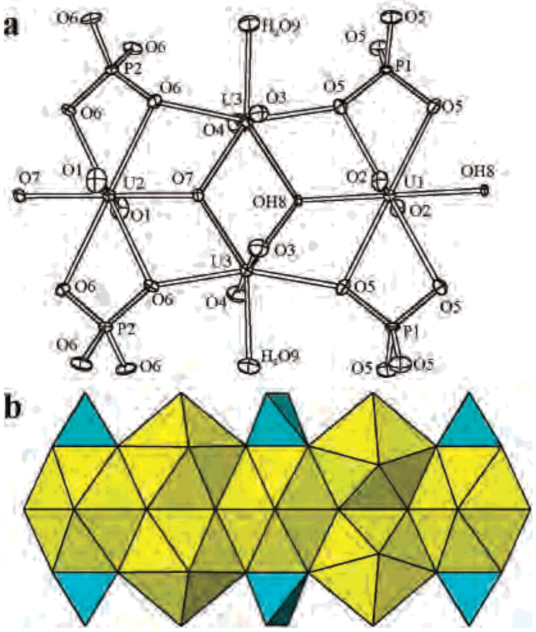

Figure 1. The chain of uranyl and phosphate tetrahedra in the structure of $[(UO_2)_3(PO_4)O(OH)(H_2O)_2](H_2O)$ (**1**) with ball-and-stick (a) and polyhedral (b) representations (ellipsoids are drawn at 50% probability level)

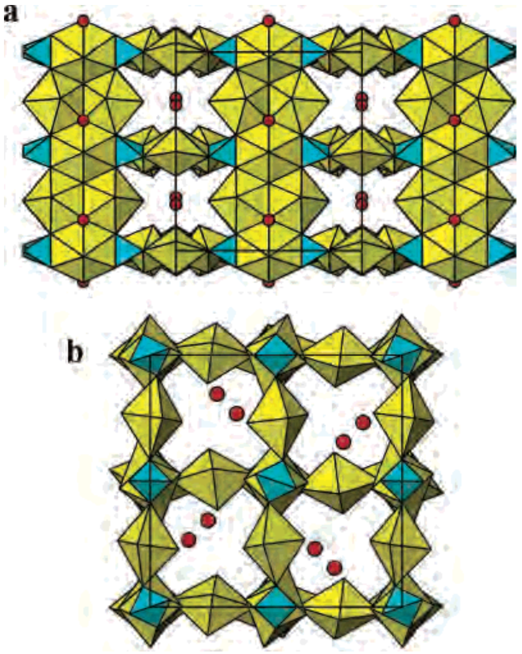

Figure 2. Polyhedral representation of the framework structure of $[(UO_2)_3(PO_4)O(OH)(H_2O)_2](H_2O)$ projected along [100] (a) and [001] (b) (legend: UO_7 polyhedra = yellow; PO_4 tetrahedra = blue).

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(14) An infrared spectrum for **1** was collected over the range 700−4000 cm^{-1} using a SensIR IlluminatIR spectrometer with a diamond ATR fitted to an Olympus microscope. The spectrum is the average of 120 scans.

(15) Crystallographic data for $[(UO_2)_3(PO_4)O(OH)(H_2O)_2](H_2O)$ (**1**): tetragonal, $P4_2/mbc$, $a = 14.015(1)$ Å, $c = 13.083(2)$ Å, $V = 2575.6(4)$ $Å^3$, $Z = 8$. Crystal dimensions: $0.07 \times 0.02 \times 0.02$ mm^3; $d_{calcd} = 5.092$ $g \cdot cm^{-3}$, $\mu = 379.1$ cm^{-1}. Data collection: Bruker SMART APEX CCD diffractometer, 39773 total reflns, 2831 unique reflns, 1383 unique reflns $I \geq 2\sigma_I$. The effects of absorption were accounted for analytically. The structure was solved by direct methods and refined to R1 = 0.034, wR2 = 0.054, $S = 0.75$ with anisotropic displacement parameters for all atoms except O10, which corresponds to a H_2O group located in the channel of the structure.

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Table 1. Selected Bond Distances (Å) for $(UO_2)_3(PO_4)O(OH)(H_2O)_2](H_2O)$ (**1**)[a]

U1-O2	1.755(7)	U3−O3	1.752(6)
U1−O2a	1.755(7)	U3−O4	1.759(5)
U1−OH8	2.341(7)	U3−O7	2.245(4)
U1−OH8a	2.341(7)	U3−O6	2.364(5)
U1−O5	2.586(6)	U3−O5	2.412(5)
U1−O5a	2.586(6)	U3−OH8	2.422(4)
U1−O5b	2.586(6)	U3−H_2O9	2.440(5)
U1−O5c	2.586(6)	P1−O5	1.537(5)
U2−O1	1.772(8)	P1−O5e	1.537(5)
U2−O1d	1.772(8)	P1−O5f	1.537(5)
U2−O7	2.240(7)	P1−O5g	1.537(5)
U2−O7d	2.240(7)	P2−O6	1.539(5)
U2−O6	2.608(6)	P2−O6e	1.539(5)
U2−O6c	2.608(6)	P2−O6h	1.539(5)
U2−O6d	2.608(6)	P2−O6i	1.539(5)
U2−O6e	2.608(6)		

[a] a = $-x + 1, -y, -z$; b = $-x + 1, -y, z$; c = $x, y, -z$; d = $-x, -y, -z$; e = $-x, -y, z$; f = $y + ^1/_2, x - ^1/_2, -z + ^1/_2$; g = $-y + ^1/_2, -x + ^1/_2, -z + ^1/_2$; h = $y, -x, -z + ^1/_2$; i = $-y, x, -z + ^1/_2$.

adjacent uranyl polyhedra as well as O10, which is an H_2O group located in the channels of the structure. H bonds extending from O10 may be accepted by any of four O_{Ur} anions of adjacent uranyl polyhedra. Bond lengths are provided in Table 1.

Uranyl phosphate minerals of the phosphuranylite group involve chains of uranyl pentagonal and hexagonal bipyramids and phosphate tetrahedra similar to those found in **1**, but linked into sheets by the sharing of polyhedra vertices and edges. In most phosphuranylite-group structures, low-valence cations and H_2O groups occupy the interlayer region and provide the only linkages between sheets. In the structures of phosphuranylite, $KCa(H_3O)_3(UO_2)[(UO_2)_3(PO_4)_2O_2]_2(H_2O)_8$,[17] and vanmeersscheite, $U(OH)_4[(UO_2)_3(PO_4)_2(OH)_2]_2(H_2O)_4$,[18] linkage of the uranyl phosphate sheets is through uranyl polyhedra located in the interlayer, resulting in framework structures, although the structural connectivity is dominated by the presence of uranyl phosphate sheets.

Recently, uranyl phosphate frameworks have been described in the structures of $(UO_2)_3(PO_4)_2(H_2O)_4$[11] and $A_2(UO_2)[(UO_2)(PO_4)]_4(H_2O)_2$ (A = Cs, Rb, K).[12] Each involves uranyl phosphate sheets that are based upon the uranophane anion topology,[2] in which uranyl pentagonal bipyramids share edges to form chains one polyhedron wide, which are linked into sheets by sharing of vertices and edges with phosphate tetrahedra. The resulting uranyl phosphate sheets are linked to uranyl polyhedra located in the interlayer of the structures, resulting in a framework of polyhedra of high bond valence. In these structures, phosphate tetrahedra are linked to three uranyl polyhedra, one by sharing an edge, and two only by sharing of vertices, in contrast to the connectivity in **1**. Although these compounds possess framework structures, their connectivities are dominated by sheets of polyhedra, as is typical for uranyl compounds.

The linkage of phosphuranylite-type uranyl phosphate chains in the structure of **1** into an open framework is unprecedented in minerals and synthetic compounds. Previously, these uranyl phosphate chains were only known to occur in structures involving linkage of the chains into sheets, with cations in the interlayer regions providing for the charge neutrality of the structure. In contrast, the framework of **1** is electroneutral, and the only constituents in the channels through the framework are H_2O. It seems reasonable to expect that a new family of related uranyl phosphate framework materials may be obtained, as replacement of the OH8 group, which is bonded to three U^{6+} cations, with an O atom that would permit insertion of cations within the channels in the framework. The new mode of connection of uranyl phosphate chains observed in **1** also suggests that a family of microporous uranyl phosphate framework materials may exist. Such structures could contain bands composed of two or more uranyl phosphate chains linked parallel to the equatorial planes of the uranyl polyhedra, with three-dimensional linkage of the bands in two opposing directions forming a framework.

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Supporting Information Available: X-ray crystallographic data in CIF format and an infrared spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

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