

Expanding the Crystal Chemistry of Actinyl Peroxides: Open Sheets of Uranyl Polyhedra in $\text{Na}_5[(\text{UO}_2)_3(\text{O}_2)_4(\text{OH})_3](\text{H}_2\text{O})_{13}$

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A uranyl peroxide, $\text{Na}_5[(\text{UO}_2)_3(\text{O}_2)_4(\text{OH})_3](\text{H}_2\text{O})_{13}$, with an open sheet of uranyl polyhedra has been synthesized under ambient conditions and structurally characterized. The structure (orthorhombic, *Cmca*, $a = 23.632(1) \text{ \AA}$, $b = 15.886(1) \text{ \AA}$, $c = 13.952(1) \text{ \AA}$, $V = 5237.7 \text{ \AA}^3$, and $Z = 8$) consists of sheets composed of two symmetrically unique uranyl $(\text{UO}_2)^{2+}$ ions that are coordinated equatorially by two peroxide groups and two OH^- groups, forming distorted uranyl hexagonal bipyramids of composition $(\text{UO}_2)(\text{O}_2)_2(\text{OH})_2^{4-}$. The uranyl bipyramids are connected into sheets with openings with dimensions 13.7 \AA along $[010]$ and 15.9 \AA along $[100]$. The shortest dimension of the cavity is 8.08 \AA . Sheets of two-dimensionally polymerized uranyl polyhedra are the most common structural type of inorganic uranyl phases; however, such an open topology has never been observed.

Recent advances in the crystal chemistry of hexavalent uranium have been driven by the search for novel solids with important materials properties,¹ as well as the likely impact of uranyl phases upon the mobility of radionuclides in a geological repository for nuclear waste and in vadose zones contaminated by actinides.² The crystal chemistry of U^{6+} is richly diverse, with more than 350 inorganic structures now known.³ The U^{6+} cation is almost invariably present in crystal

structures as part of an approximately linear $(\text{UO}_2)^{2+}$ uranyl ion, and the uranyl ion is coordinated by four, five, or six ligands arranged at the equatorial vertexes of square, pentagonal, or hexagonal bipyramids, respectively. Linkage of uranyl polyhedra, with either other uranyl polyhedra or other polyhedra containing cations of higher valence, is common, and sheets of polyhedra tend to dominate because of the uneven distribution of bond strengths within uranyl polyhedra.⁴ The resulting sheets can be highly complex and can have primitive repeat distances that exceed 50 \AA .⁵ Burns³ reviewed the structures of 204 uranyl compounds that contain sheets of polyhedra. Notably, small voids are often present in such sheets, but none are known that contain voids exceeding $\sim 5 \text{ \AA}$ in minimum dimension.

The crystal chemistry of actinyl peroxides formed under alkaline conditions has been largely overlooked by previous researchers. Whereas various actinyl peroxide crystals have reportedly formed from alkaline solutions,⁶ essentially none of their structures have been studied. Very recently, spherical nanoclusters containing 24, 28, and 32 uranyl peroxide polyhedra that formed in alkaline solutions have been isolated and structurally characterized.⁷ These clusters self-assemble in solution prior to crystallization. Each contains uranyl peroxide hexagonal bipyramids, with peroxide groups forming two or three of the polyhedron edges. Shortening of the polyhedron edges associated with the peroxide groups is thought to favor the formation of these clusters.⁷ Prior to the discovery of the spherical nanoclusters, the mineral studtite, $\text{UO}_2(\text{O}_2)(\text{H}_2\text{O})_4$, was the only inorganic compound known to contain uranyl peroxide polyhedra that share polyhedral elements.⁸ Changing the shapes of uranyl bipyramids by inclusion of peroxide groups promotes linkages into

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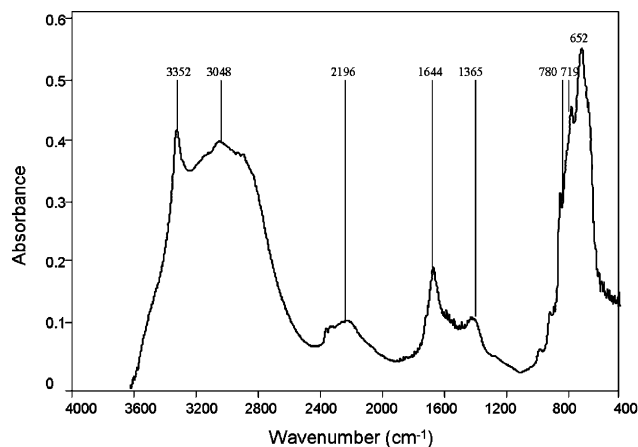


Figure 1. IR spectrum of **1**.

novel structural units, and actinyl peroxides potentially possess a wealth of unprecedented structures.

We are exploring the crystal chemistry of actinyl peroxides that form under alkaline conditions.⁷ As part of this program of research, we have reacted uranyl nitrate with peroxide and alkali hydroxides at ambient temperature and pressure. The presence of strong bases results in vigorous exothermic reactions and the self-catalyzed breakdown of H₂O₂ to form H₂O liquid and O₂ gas. In the presence of sodium hydroxide, reactions result in yellow crystals of Na₅[(UO₂)₃(O₂)₄(OH)₃](H₂O)₁₃ (**1**) up to 100 μm in maximum dimension.⁹ These crystals rapidly degrade in air but were stabilized in a stream of N₂ at 100 K for data collection.

The IR spectrum of **1** (Figure 1) indicates that ν₃(UO₂)²⁺ is observed as a dominant band at 719 cm⁻¹, while ν₁(UO₂)²⁺ is a shoulder at 780 cm⁻¹.¹⁰ Bands in the range of 2800–3352 cm⁻¹ are associated with H-bonded H₂O groups. The band near 1644 cm⁻¹ is probably a combination of bending modes for H₂O groups. The origin of the bands at 652 and 1365 cm⁻¹ is uncertain; they may be due to some combination of H₂O liberation modes and Na–O vibrations.

Single-crystal X-ray diffraction data revealed that **1** crystallizes in space group *Cmca* and that the structure has a remarkable new type of open sheet of uranyl polyhedra.¹¹ The structure contains two symmetrically unique U⁶⁺ posi-

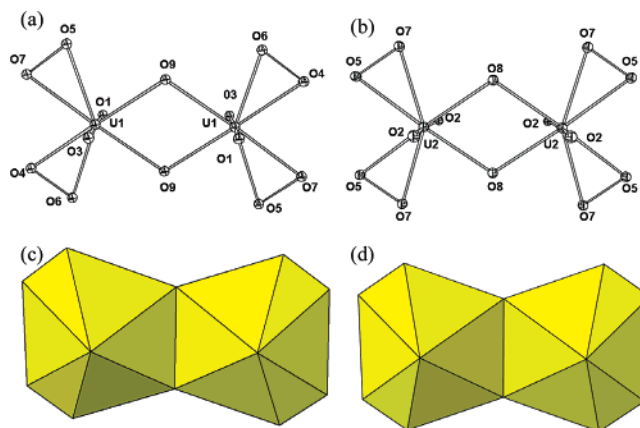


Figure 2. Dimers of polyhedra with composition (UO₂)₂(O₂)₄(OH)₂ in **1**: (a) ball-and-stick representation of U1; (b) ball-and-stick representation of U2; (c) polyhedral representation of U1; (d) polyhedral representation of U2. The O5–O7 and O4–O6 bond distances are 1.49(1) and 1.47(1) Å, respectively, causing a distortion of each uranyl hexagonal bipyramid.

tions, each of which is strongly bonded to two O atoms, forming uranyl ions. The U1 uranyl ion O–U–O bond angle is 178.0(4)°, with U–O bond lengths of 1.793(9) and 1.820(9) Å. The U2 uranyl ion O–U–O angle is more strongly distorted to 171.3(5)°, and the U–O bond lengths are 1.829(9) Å. Each of the uranyl ions is coordinated by two hydroxyl groups and two peroxide groups (Figure 2), resulting in hexagonal bipyramids in which two of the equatorial edges correspond to peroxide groups. Topologically and chemically identical polyhedra were found earlier connected into spherical nanoclusters containing 24 and 32 uranyl polyhedra.⁷ The equatorial bond lengths of the polyhedra range from 2.314(9) to 2.433(9) Å for U1 and from 2.350(9) to 2.379(8) Å for U2, which are in agreement with those expected for well-refined structures.⁴ The O–O bond lengths of the peroxide groups are 1.47(1) and 1.49(1) Å, for O4–O6 and O5–O7, respectively, corresponding to a significant shortening of these edges of the uranyl hexagonal bipyramids relative to uranyl hexagonal bipyramids that contain no peroxide.

Uranyl peroxide hexagonal bipyramids are linked into unusual open sheets in the structure of **1** (Figure 3). Two U1 bipyramids share an OH–OH edge, giving a dimer with composition [(UO₂)(O₂)₂(OH)]₂⁶⁻. Similarly, pairs of U2 bipyramids are linked to form a dimer with the same composition (Figure 2). Each dimer of bipyramids contains four peroxide edges. In the case of the U1 dimers, two of these edges are shared with adjacent U2 dimers, whereas all four of the peroxide edges of the U2 dimers are shared with U1 dimers. The resulting two-dimensional sheet has composition [(UO₂)₃(O₂)₄(OH)₃]⁵⁻ (Figure 3).

There are four symmetrically independent Na positions in the structure that are coordinated by six ligands each. The sheets of composition [(UO₂)₃(O₂)₄(OH)₃]⁵⁻ are stacked along [001] (Figure 4), with linkages provided by the Na cations and eight symmetrically independent H₂O groups in the interlayer region. The Na and H₂O groups exhibit displacement parameters that are significantly larger than those for atoms in the structural unit, indicating some positional

(9) Single crystals of **1** were prepared by slow addition of a 5 M solution of sodium hydroxide (1 g of NaOH in 10 mL of H₂O) to 1 mL of a 2 M uranyl nitrate solution (1 g of UO₂NO₃(H₂O)₆ in 1 mL of H₂O) to adjust the pH to 12.82. A total of 1 mL of 30% H₂O₂ is added dropwise. This self-catalytic exothermic reaction results in significant off-gassing of O₂. After 10 days at ambient temperature and pressure, crystals were removed from the red solution.

(10) Single crystals of **1** were isolated on a glass slide and placed on a SensIR technologies IlluminatIR. The absorbance was recorded using a diamond ATR objective as a function of the wavenumber. Spectra were averaged for 120 measurements per crystal and averaged for four crystals.

(11) Crystallographic data for **1**: Na₅[(UO₂)₃(O₂)₄(OH)₃](H₂O)₁₃, yellow, crystal dimensions 80 × 80 × 20 μm, orthorhombic, *Cmca*, *Z* = 8, *a* = 23.632(1) Å, *b* = 15.886(1) Å, *c* = 13.952(1) Å, *V* = 5237.7(7) Å³, *μ* = 18.71 cm⁻¹, *D*_{calc} = 3.394 g/cm³, *R*₁ = 0.0556, and *wR*₂ = 0.1566. Data collection: Bruker SMART APEX CCD diffractometer, *T* = 100 K, Mo Kα (*λ* = 0.710 73 Å), 52 295 total reflections, 5628 unique reflections, and 2501 unique reflections for *I* ≥ 4σ₁. The data were corrected for Lorentz–polarization effects and for absorption; the structure was solved by direct methods and refined on the basis of *F*² by full-matrix least squares by 94 parameters.

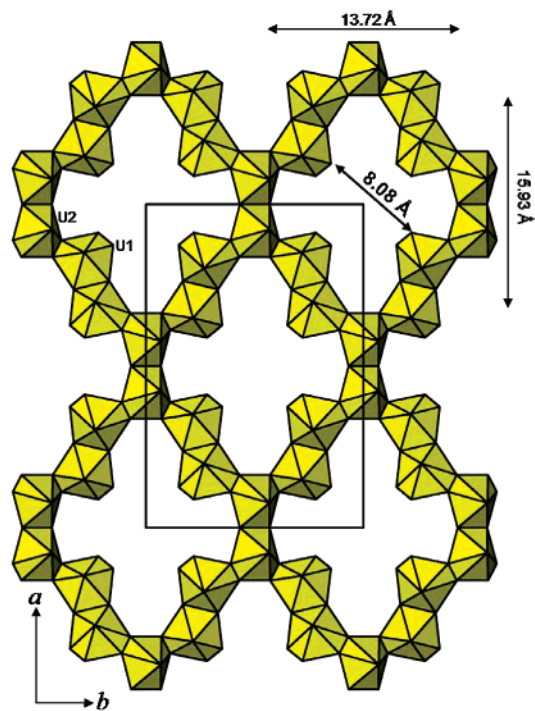


Figure 3. Microporous sheets in the structure of **1**. H₂O molecules and Na polyhedra are omitted for clarity. U1 and U2 dimers are interconnected by sharing equatorial peroxide edges. Each U2 dimer shares all four equatorial peroxide edges with four U1 dimers. Dimers of U1 uranyl polyhedra share two opposite equatorial peroxide edges with two dimers of U2 uranyl polyhedra.

disorder. Furthermore, the Na4 atoms are distributed over two closely spaced sites, and locally only one of these is occupied.

The openings in the sheets of the structure of **1** are of particular interest because of the size of the cavity, 13.72 Å along [010] and 15.93 Å along [100], as measured from the centers of the bounding O atoms. The shortest dimension of the cavity, from terminal peroxide anions of U1, is 8.08 Å. Linkage of uranyl polyhedra into two-dimensional sheets containing pores of comparable size is unknown in uranyl compounds. Formation of this sheet topology is perhaps precluded in the case of equilateral uranyl polyhedra.

The structure of **1** further demonstrates the rich solid-state chemistry of actinyl peroxides grown from alkaline solutions.

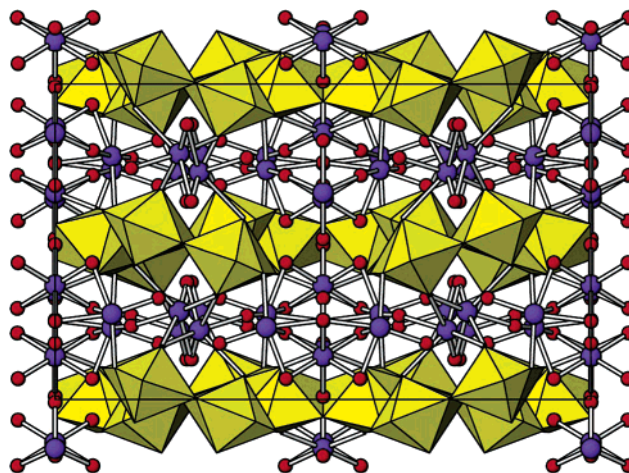


Figure 4. Interconnectivity of the microporous sheets in the structure of **1** viewed down [010]: yellow, U polyhedra; red, H₂O groups; blue, Na⁺.

From a bond-valence perspective, the sharing of a peroxide group between two uranyl hexagonal bipyramids, as an equatorial edge, results in a stable configuration. For example, consider the (O₂)²⁻ group in the structure of **1** that is composed of O5 and O7. The O5 atom is bonded to U1 and U2 with bond lengths of 2.433(9) and 2.355(8) Å, respectively, which correspond to 0.46 and 0.54 valence units (vu), respectively.^{4b} The O7 atom is bonded to U1 and U2 with bond lengths of 2.414(9) and 2.350(9) Å, respectively, corresponding to 0.48 and 0.54 vu, respectively.^{4b} The total bond valence incident upon the peroxide group from the U⁶⁺–O bonds is therefore 2.02 vu, which is close to its formal valence of 2.

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Supporting Information Available: A file of X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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