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Expanding the Crystal Chemistry of Actinyl Peroxides: μ-η^2:η^1 Peroxide Coordination in Trimers of U^{6+} Polyhedra

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Uranyl peroxides have been intensively studied recently because they form topologically complex structures including spherical clusters containing tens of uranyl polyhedra. In all uranyl peroxides reported to date, the coordination of U^{6+} cations by peroxide is bidentate. The compound $K_2(Mg(H_2O)_6)_4[(UO_2)_3(O_2)_8]\cdot 2H_2O$ has been synthesized and characterized and contains a trimer of linked uranyl peroxide polyhedra. The central U^{6+} cation is linked to two peroxide groups in a μ-η^2:η^1 configuration. Inclusion of this mode of linkage could dramatically increase the flexibility and topological complexity of uranyl peroxide nanoscale clusters.

We are conducting a systematic study of uranyl peroxide structural topologies and reported the self-assembly of uranyl peroxide polyhedra into approximately spherical nanoscale clusters containing 24, 28, 32,[1] 40, and 50[2] polyhedra. The first structure of a uranyl peroxide was reported for $Na_4[(UO_2)(O_2)_3](H_2O)_9$,[3] which contains uranyl hexagonal bipyramids, with three equatorial edges being bidentate peroxide groups. The polyhedra, with composition $(UO_2)(O_2)_3$, are linked by bonds to Na and by H bonds. The second uranyl peroxide structure was reported for the mineral studtite, $[(UO_2)(O_2)_2(H_2O)_2]$, in 2003.[4] It contains uranyl hexagonal bipyramids with two edges defined by bidentate peroxide in a trans configuration and two equatorial ligands being H_2O. The bipyramids are linked into chains by sharing the peroxide edges. We reported that $Na_5[(UO_2)_3(O_2)_4(OH)_3](H_2O)_{13}$ contains open sheets of uranyl peroxide polyhedra[5] and several compounds with either isolated uranyl hexagonal bipyramids with three bidentate peroxide or dimers of uranyl hexagonal bipyramids with two bidentate peroxide each and a common edge defined by two hydroxyl groups.[6] Also, uranyl peroxide polyhedra containing both bidentate peroxide and carbonate groups have been reported.[7,8] Thus, uranyl peroxide structures to date contain a U^{6+} cation that is coordinated by bidentate peroxide ligands, and in many cases, an edge defined by peroxide is shared with other uranyl polyhedra, leading to structural topologies that depart dramatically from other inorganic U^{6+} compounds.[1,2] We note that μ-η^2:η^1 peroxide linkages have been reported in homodinuclear complexes containing V^{5+},[9] Rh^{1+},[10] and Pd^{2+}[11] and in heterodinuclear complexes containing Fe^{3+} and Cu^{2+}[12] but have not been previously reported in actinyl peroxides. Here we report the structure of $K_2(Mg(H_2O)_6)_4[(UO_2)_3(O_2)_8]\cdot 2H_2O$ (**1**) with the first example of a U^{6+} cation with a μ-η^2:η^1 (or end-on) peroxide ligand and discuss the distribution of bond lengths in uranyl peroxide polyhedra.

Crystals of **1** formed following heating of an alkaline solution containing uranyl nitrate, magnesium sulfate, potassium hydroxide, and peroxide to 70 °C.[13] Yellow, lathlike crystals 300 μm in length were obtained in low yield. A suitable crystal was selected for X-ray diffraction study at

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(13) Crystals of **1** were synthesized by adding 0.1973 g of $MgSO_4$ to 4 mL of a 203 mM uranyl nitrate hexahydrate aqueous solution. A total of 0.5 mL of 30% H_2O_2 was added, and a yellow precipitate formed. A total of 1 mL of 3.0 M LiOH was added, and the solution was stirred vigorously. The precipitate dissolved, and a clear burnt-orange solution formed that was left uncovered for 24 h under ambient conditions, after which 1 mL was placed in a 5 mL Teflon vial with the addition of 6.5 μL of 3 M KOH. The vial was placed in a Teflon-lined autoclave with 30 mL of water for counterpressure and heated at 70 °C for 24 h. After cooling to room temperature, the solution was transferred to a 4 mL glass vial, capped, and stored at room temperature for 6 weeks, after which lath-shaped crystals approximately 300 μm in length were collected.

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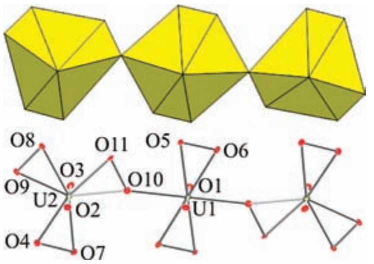

Figure 1. Polyhedral (top) and ellipsoidal (70% probability) representations of the trimer of uranyl peroxide polyhedra in **1**.

110 K.[14] An IR spectrum of a crystal of **1** was obtained using an attenuated total reflectance objective and a microspectrometer (see the Supporting Information).

The structure of **1** contains two symmetrically distinct U^{6+} cations, both of which are present as $(UO_2)^{2+}$ uranyl ions with O−U−O angles of 180.0 and 178.0(2)° for U1 and U2, respectively, and with bond lengths ranging from 1.837(1) to 1.845(1) Å (Figure 1). The U1 uranyl ion is coordinated by two bidentate peroxide groups in a trans arrangement similar to that in the structure of studtite,[4] as well as two O atoms of μ-η^2:η^1 peroxide coordination. The U−O bond lengths to the bidentate peroxide O atoms range from 2.277(4) to 2.284(4) Å, whereas that to the O atom of the μ-η^2:η^1 peroxide is 2.438(4) Å. Peroxide O−O bond lengths range from 1.486(5) to 1.501(3) Å, which are within the typical range. The U2 uranyl ion is coordinated by three bidentate peroxide groups, with bond lengths ranging from 2.285(4) to 2.334(4) Å. The structure also contains three Mg cations, each of which is coordinated octahedrally by six H_2O groups with bond lengths ranging from 2.039(4) to 2.110(4) Å. The single K atom is coordinated by four uranyl ion O atoms, two peroxide group O atoms, and three H_2O groups with distances ranging from 2.712(4) to 3.246(4) Å.

The U1 cation is located on a center of symmetry, and its polyhedra share a single vertex with U2 polyhedra on either side, resulting in a unique trimer of polyhedra (Figure 1). The linkage between the U1 and U2 polyhedra is highly unusual because the O10−O11 peroxide group is bidentate to U2 but is only one-connected to U1. This is the only known structure that contains a U^{6+} polyhedron with μ-η^2:η^1 peroxide coordination and is also the first structure that contains a structurally isolated trimer of uranyl peroxide polyhedra.

The structure of **1** (Figure 2) includes an extensive network of H bonds that are donated by the single H_2O group that is held in the structure by H bonding only and the H_2O groups that coordinate the Mg cations. With the exception of the O10 atom, which is shared between U1 and U2, all of the peroxide groups and uranyl ion O atoms in the trimer of polyhedra accept H bonds. Several of these anions are also bonded to the K atom. The trimers of uranyl polyhedra extend along [001] and are linked along [100] through the K sites as well as in all directions by H bonds (Figure 2).

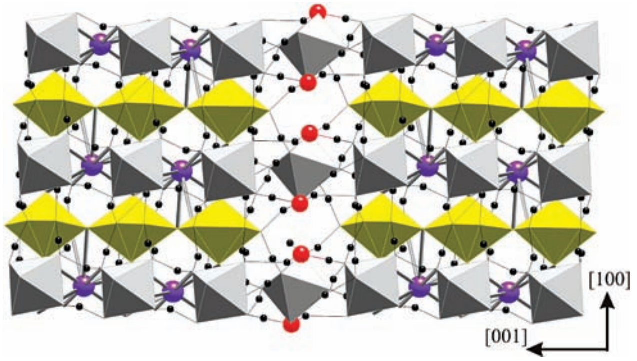

Figure 2. Polyhedral and ball-and-stick representation of the structure of **1**. U and Mg polyhedra are shown in yellow and gray, respectively. K atoms are shown by blue spheres. Black circles indicate the locations of H atoms, and thin black lines show their bonds. The O atom of O12, which is held in the structure by H bonds only, is shown as a red circle.

The $(UO_2)^{2+}$ uranyl ion is very important in the nuclear energy cycle and is highly stable in general.[15] The observation that the uranyl ion bond lengths in **1** are significantly longer than the typical value of 1.78 Å in well-refined structures containing hexagonal bipyramids[16] suggests that coordination by peroxide may reduce the strength of the uranyl bonds. Likewise, the uranyl ion bond lengths reported in three $(UO_2)(O_2)_3$ clusters[6] are in the range of 1.823(5)−1.847(2) Å, those in a $(UO_2)(O_2)(OH)_2$ cluster are 1.88(1) Å,[6] and those in $(UO_2)(O_2)(CO_3)_2$ species are in the range of 1.81(1)−1.827(8) Å.[7,8] Yet, in isolated $(UO_2)(CO_3)_3$ clusters, the uranyl ion presents a typical length.[17−19] Coordination of the uranyl ion by peroxide in solids with isolated clusters results in a significant increase of the uranyl ion bond lengths. This suggests that the U^{6+}−peroxide interactions are not purely ionic, as is generally thought to be the case between uranyl ions and equatorial ligands of bipyramids. High-level quantum calculations are needed to develop an understanding of the role of coordinating peroxide in the uranyl ion properties.

The bond valence sums for U1 and U2, calculated using coordination-specific parameters,[20] are 6.38 and 6.50 valence units (vu), respectively. These are much higher than the expected value of 6.0 vu, although the coordination-specific parameters usually give sums close to 6.0 vu.[20]

Incident bond valence sums on O atoms of the uranyl polyhedra, neglecting contributions from U^{6+}, were calcu-

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(14) 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 4.67 cm. A sphere of data was collected using framewidths of 0.3° in ω at 110 K. Intensity data were corrected for Lorentz, polarization, and background effects using the Bruker program *APEX II*. A semiempirical correction for absorption was applied using the program *SADABS*. The *SHELXTL* version 5 series of programs was used for the solution and refinement of the crystal structures. Crystal dimensions 80 × 50 × 30 μm, triclinic, $P\bar{1}$, $a = 6.5554(18)$ Å, $b = 8.2865(18)$ Å, $c = 18.146(5)$ Å, $\alpha = 95.064(5)°$, $\beta = 93.359(4)°$, $\gamma = 94.770(3)°$, $V = 976.3(4)$ Å^3, R1 = 3.50%, wR2 = 7.22%, 17 278 total reflections, 6385 unique reflections, 5171 unique reflections, $F_o \geq 4\sigma$.

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Table 1. Summary of Bond Valence Sums Incident upon O Atoms of Uranyl Polyhedra in **1**

	$BV_{structure}$	$BV_{calculated}$	ΔBV
U1−O1 ×2	1.52	1.49	−0.03
U1−O5 ×2	0.42	0.63	0.21
U1−O6 ×2	0.53	0.62	0.09
U1−O10 ×2	0.43	0.46	0.03
U2−O2	1.59	1.50	−0.09
U2−O3	1.53	1.48	−0.05
U2−O4	0.45	0.57	0.12
U2−O7	0.47	0.57	0.10
U2−O8	0.52	0.60	0.08
U2−O9	0.42	0.60	0.18
U2−O10	0.51	0.57	0.06
U2−O11	0.48	0.62	0.14

lated using K−O distances[21] and O−O separations in the case of H bonds.[22] The uranyl polyhedra are shown in Figure 1, with the bond valence sums incident upon each O atom from the extended structure given in Table 1. The formal valences of the O atoms are taken as −2 and −1 for uranyl ion O atoms and peroxide O atoms, respectively, as the peroxide entity has a formal valence of −2. The difference between the formal valence for each O atom and that incident upon it from the extended structure can then be attributed to the bond to U^{6+} and is designated $BV_{structure}$. The resulting values of $BV_{structure}$ are compared to those calculated using the bond lengths and bond-valence parameters (designated $BV_{calculated}$) in Table 1. Subtraction of $BV_{structure}$ from the formal valences of the O atoms provides the total bond valence available for bonds to U^{6+}. This value is approximately 5.80 vu for each of U1 and U2, with some uncertainty arising from the distribution of valences from O10 to U1 and U2.

For the O atoms of uranyl ions, the $BV_{structure}$ values are consistently larger than $BV_{calculated}$ by 0.03−0.09 vu. There is a much larger discrepancy between $BV_{structure}$ and $BV_{calculated}$ for the O atoms of the peroxide groups, and in all cases, $BV_{structure}$ values are the smallest, with a maximum deviation of 0.21 vu. The deviation is the least for the O10−O11 peroxide group, of which the O10 atom is shared between U1 and U2. The bond-valence parameters derived for $U^{6+}-O^{2-}$ are apparently not appropriate for U^{6+}−peroxide interactions, and new parameters for this type of interaction are needed. Bonds between U^{6+} and peroxide O atoms are significantly shorter than those found for $U^{6+}-O^{2-}$, yet their bond valence sums are not as high as predicted by the bond-valence parameters.

The structure of **1** demonstrates a new type of U^{6+}−peroxide linkage. This linkage may prove important in understanding the structures and properties of aqueous uranyl peroxide species. The potential of incorporation of this type of linkage into nanoclusters built from uranyl peroxide polyhedra would add another dimension of topological complexity and potential for chemical tuning.

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Supporting Information Available: Crystallographic data in CIF format and the IR spectrum for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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