Bonding Properties of a Novel Inorganometallic Complex Ru(SnPh3)2(CO)2(iPr-DAB) (iPr-DAB = N,N'-Diisopropyl-1,4-diaza-1,3-butadiene) and its Stable Radical-Anion, Studied by UV-Vis, IR and EPR Spectroscopy, (Spectro)Electrochemistry, and Density Functional Calculations


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

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A uranyl peroxide, Na$_5$[(UO$_2$)$_3$(O$_2$)$_4$(OH)$_3$](H$_2$O)$_{13}$, with an open sheet of uranyl polyhedra has been synthesized under ambient conditions and structurally characterized. The structure (orthorhombic, Cmca, $a = 23.632(1)$ Å, $b = 15.886(1)$ Å, $c = 13.952(1)$ Å, $V = 5237.7$ Å$^3$, and $Z = 8$) consists of sheets composed of two symmetrically unique uranyl (UO$_2$)$_{2}^{2+}$ ions that are coordinated equatorially by two peroxide groups and two OH$^-$ groups, forming distorted uranyl hexagonal bipyramids of composition (UO$_2$)$_2$(O$_2$)$_2$$(OH)_2^{4-}$. The uranyl bipyramids are connected into sheets with openings with dimensions 13.7 Å along [010] and 15.9 Å along [100]. The shortest dimension of the cavity is 8.08 Å. 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 of uraniferous rocks.$^2$ The crystal chemistry of U(VI) is richly diverse, with more than 350 inorganic structures now known.$^1$ The U(VI) cation is almost invariably present in crystal structures as part of an approximately linear (UO$_2$)$_{2}^{2+}$ 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.$^2$ The resulting sheets can be highly complex and can have primitive repeat distances that exceed 50 Å.$^3$ Burns$^3$ 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 ~5 Å 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,$^4$ 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.$^5$ These clusters self-assemble in solution prior to crystallization. Each contains uranyl peroxide hexagonal bipyramids, with peroxide groups forming two or three of the polyhedral edges. Shortening of the polyhedral 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, UO$_2$(O$_2$)(H$_2$O)$_4$, was the only inorganic compound known to contain uranyl peroxide polyhedra that share polyhedral edges.$^6$ Changing the shapes of uranyl bipyramids by inclusion of peroxide groups promotes linkages into

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We are exploring the crystal chemistry of actinyl peroxides that form under alkaline conditions. 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 which are associated with H-bonded H₂O groups. The origin of the bands at 652 and 1365 cm⁻¹ is uncertain; they may be due to some 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 bending modes for H₂O groups.

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. The structure contains two symmetrically unique U₆ polyhedra range from 2.314(9) to 2.433(9) Å for U1 and 2.350(9) to 2.379(8) Å for U2, which are in agreement with those expected for well-refined structures. 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)]⁺. 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)(O₂)₂(OH)]⁺ (Figure 3).

There are four symmetrically independent Na positions in the structure that are coordinated by six ligands each. The sheets of composition [(UO₂)(O₂)₂(OH)]⁺ 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

![Figure 1: IR spectrum of 1.](image)

![Figure 2: Dimers of polyhedra with composition (UO₂)(O₂)₂(OH) in I: (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.](image)
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.

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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.