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COMMUNICATIONS

Published on Web 10/30/2009

Uranyl−Peroxide Interactions Favor Nanocluster Self-Assembly

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Uranium is the heaviest abundant element,[1] is the fuel of nuclear reactors, and is a troublesome environmental contaminant in many locations. There is currently much interest in the development of greener nuclear fuel cycles that produce more energy from a unit of uranium, without a proportional increase in waste production. The linear $(UO_2)^{2+}$ uranyl ion is central to the chemistry of this unusual element, and several recent reports focus on unexpected reactions involving this normally unreactive functional group.[2] We earlier reported the self-assembly of uranyl polyhedra containing peroxide under ambient conditions into a complex family of closed clusters, some with fullerene topologies, containing as many as 60 uranium atoms.[3,4] Inclusion of peroxide along equatorial edges of uranyl bipyramids disrupts their tendency to form infinite sheets, although it remains unclear why peroxide causes such a dramatic departure from conventional U^{6+} structural chemistry. An understanding of the role of peroxide in cluster formation is central to designing synthesis approaches to tune the size and topology of these clusters.

Designer control of actinide materials at the nanoscale presents exciting opportunities in the reprocessing of nuclear fuels and as precursors in the synthesis of a broad range of fuels and waste forms. Uranyl peroxide hydroxide polyhedra self-assemble under favorable conditions to form closed clusters containing 24, 28, 32, 36, 40, 44, 50, and 60 uranyl polyhedra[3,4] (designated U_n). Some of these have fullerene topologies with 12 pentagons as well as hexagons. The largest, U_{60}, adopts the same topology as C_{60} Buckminster fullerene with 12 isolated pentagons and 20 hexagons. Unlike carbon fullerenes, uranyl peroxide fullerenes tend to adopt the topology with the highest symmetry regardless of the presence of pentagonal adjacencies, presumably because this distributes structural strain most evenly over the cluster.[4] Uranyl peroxide hydroxide clusters can also contain topological squares, giving many more possible isomers than in the case of fullerene topologies alone.

The self-assembly of uranyl peroxide hydroxide polyhedra into polyoxometalate clusters is unique in actinide chemistry. Within these polyhedra, the bonds of the linear $(UO_2)^{2+}$ uranyl ion are strong. The uranyl ion is normally coordinated by four, five or six ligands arranged at the equatorial vertices of square, pentagonal, or hexagonal bipyramids. Where the equatorial ligands are O or OH, linkage of uranyl bipyramids by sharing equatorial edges is dominant, and there is a wide variety of complex sheets.[5,6] Where the ligands are various inorganic oxyanions, extended sheets are also common.[5] It is only with the introduction of peroxide into the uranyl polyhedra that nanometer-scale closed clusters form instead of infinite sheets contained in an extended structure.

The first structure for a uranyl peroxide was reported for $Na_4[(UO_2)(O_2)_3](H_2O)_9$ in 1968 and contains an isolated uranyl triperoxide cluster.[7] The second structure of a uranyl peroxide appeared more than two decades later for the mineral studtite.[8,9] Over the past five years several uranyl peroxide compounds have been found that have simpler structures,[10−12] in addition to the complex clusters.

Uranyl polyhedra that form closed clusters have either two or three of their equatorial edges occupied by peroxide.[3,4] All known closed clusters of uranyl polyhedra contain peroxide groups that bridge between polyhedra. The insertion of peroxide groups along equatorial edges of uranyl hexagonal bipyramids encourages their self-assembly into closed clusters. The $U{-}O_2{-}U$ dihedral angle (Figure 1a) is necessarily bent in these clusters. The fundamental question concerning the origin of the family of uranyl peroxide hydroxide closed clusters concerns the origin of this bent dihedral angle. Either the angle is bent due to steric constraints needed to close the cluster or the dihedral angle is inherently bent, thus driving formation of the clusters. Here we explore this question using crystallographic studies of closed clusters, dimers, and rings of uranyl bipyramids containing peroxide.

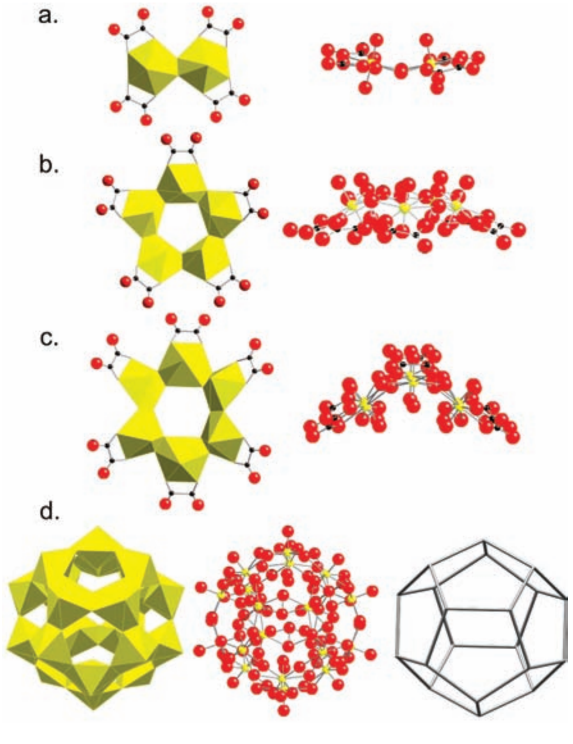

Figure 1. (a) Dimers of uranyl peroxide oxalate polyhedra in $K_6(H_2O)_4[(UO_2)_2(O_2)(C_2O_4)_4]$. (b) Five-membered rings of uranyl peroxide oxalate polyhedra in the structure of $K_{10}[(UO_2)(O_2)(C_2O_4)]_5(H_2O)_{13}$. (c) Six-membered rings of uranyl peroxide oxalate polyhedra in the structure of $Na_{12}[(UO_2)(O_2)(C_2O_4)]_6(H_2O)_{29}$. (d) Polyhedral, ball-and-stick, and polyhedral connectivity representations of the U_{20} cluster in the compound $Na_{11}(N(C_3H_7)_4)(H_2O)_9[(UO_2)_{20}(O_2)_{30}]$.

We report here isolation of a closed cluster containing 20 uranyl triperoxide polyhedra with composition $[(UO_2)_{20}(O_2)_{30}]^{20-}$ crystallized in the compound $Na_{11}(N(C_3H_7)_4)_9(H_2O)_9[(UO_2)_{20}(O_2)_{30}]$ (Figure 1d). The Na and organic cations are located inside and between

10.1021/ja907837u CCC: $40.75

the clusters, respectively. U_{20} was isolated from an alkaline solution of uranyl nitrate, NaCl, and tetrapropylammonium hydroxide, with the organic molecules acting as counterions that facilitated the crystallization of the cluster. The diameter of U_{20} is 18.0 Å, measured from the edges of bounding O atoms. The remarkable topology of U_{20} contains only pentagons, of which there are 12. This is the smallest possible fullerene topology, with ideal symmetry I_h, and is the only fullerene isomer with 20 vertices. It also has the largest number of pentagonal adjacencies of any fullerene topology. Its isolation confirms that pentagonal adjacencies are not an important factor in the stability of fullerene topologies formed by uranyl polyhedra, consistent with our earlier findings.[4]

Formation of closed clusters of uranyl polyhedra requires that dihedral angles of shared edges are bent. Comparing $U-O_2-U$ angles in eight closed clusters[3,4] with the $U-(OH)_2-U$ dihedral angles, the $U-O_2-U$ angles in a given cluster are always smaller than the $U-(OH)_2-U$ angles. The smallest cluster previously reported, U_{24}, has the smallest average dihedral angles of 135.5° and 157.8° for $U-O_2-U$ and $U-(OH)_2-U$, respectively. All shared edges in the new U_{20} cluster are peroxide, and the $U-O_2-U$ angles range from 138.5° to 142.1°. The large U_{60} cluster has average dihedral angles of 144.8° and 172.7° for $U-O_2-U$ and $U-(OH)_2-U$, respectively. Consistently tighter dihedral angles for the peroxide edges at least indicate there is less of an energetic penalty for this bending, relative to that of the hydroxyl edge, and are consistent with a bent dihedral angle being an inherent property of the uranyl−peroxide configuration.

Closed clusters consisting of uranyl peroxide hydroxide polyhedra form so readily in alkaline solutions that it is difficult to isolate fragments of these clusters in crystals. We achieved isolation of three fragments by frustrating cluster formation by addition of oxalate groups along equatorial edges of the bipyramids. These structures, reported here for the first time, provide insight into the geometry of fragments of the clusters before the steric constraints of being in a cluster are imposed.

The structure of $K_6(H_2O)_4[(UO_2)_2(O_2)(C_2O_4)_4]$ contains a dimer of uranyl peroxide oxalate polyhedra (Figure 1a) with composition $[(UO_2)_2(O_2)(C_2O_4)_4]^{6-}$. The shared edge is peroxide, and each polyhedron has two oxalate ligands in bidentate coordination to the uranium. This cluster is linked into an extended structure only through relatively weak interactions with low-valence cations. The $U-O_2-U$ angle is strongly bent at 152.9°, which is very similar to that found in $Na_2Rb_4(UO_2)_2(O_2)_5(H_2O)_{14}$.[12]

The compounds $K_{10}[(UO_2)(O_2)(C_2O_4)]_5(H_2O)_{13}$ and $Na_{12}[(UO_2)(O_2)(C_2O_4)]_6(H_2O)_{29}$ contain isolated five- and six-membered rings of uranyl peroxide oxalate polyhedra (Figure 1b,c). In both cases all of the edges that are shared between polyhedra are peroxide, and each polyhedron also contains an oxalate in bidentate coordination to uranium. These rings are topologically analogous to the five- and six-membered rings that occur in clusters of uranyl bipyramids, but here there is no steric constraint so that the $U-O_2-U$ angles depart from 180° as is the case in the closed clusters. The $U-O_2-U$ angles in the five-membered ring range from 142.5° to 158.4°, whereas those in the six-membered ring are in the range 137.5° to 144.5°. In all cases, the $U-O_2-U$ angles are sharply bent. The geometry of the five-membered ring may be compared directly with its analogue in U_{20}, in which the $U-O_2-U$ angles cluster around 140°. The range of $U-O_2-U$ angles in these rings is similar to those contained within closed clusters.

Several structures published earlier by our group provide further insight into the uranyl−peroxide interaction. In $K_6[(UO_2)(O_2)_2(OH)]_2(H_2O)_7$,[12] an isolated dimer of uranyl peroxide hydroxide polyhedra occurs, and the shared edge between the two polyhedra consists of hydroxyl. The $U-(OH)_2-U$ angle is 180°. In contrast, the dimer of uranyl peroxide polyhedra found in $Na_2Rb_4(UO_2)_2(O_2)_5(H_2O)_{14}$,[12] in which the shared edge is peroxide, has a $U-O_2-U$ angle that is sharply bent at 153.1°. The mineral studtite, $UO_2(O_2)(H_2O)_2(H_2O)_2$, contains infinite chains of uranyl hexagonal bipyramids in which peroxide groups along two of the *trans* equatorial edges of the bipyramids are shared between polyhedra along the chain length.[8] These chains are linked only through H bonds, so steric constrains on the chain conformation are minimal. The chains are distinctly corrugated, with a $U-O_2-U$ angle of 140.2°.[8] The structure of $Na_5[(UO_2)_3(O_2)_4(OH)_3](H_2O)_{13}$ contains sheets of uranyl peroxide hydroxide polyhedra with both shared peroxide and hydroxyl edges.[11] These sheets have $U-O_2-U$ and $U-(OH)_2-U$ angles of 134.8° and 180.0°, respectively.

The structural evidence presented herein strongly supports the hypothesis that the dihedral angle in the $U-O_2-U$ linkage is inherently bent. The angle is pliable to some extent, as structures have been found with angles ranging from 134.8° through 158.4°. In contrast, the dihedral angle of the uranyl−hydroxyl−uranyl linkage is 180° in the absence of steric constraints but is as bent at 157.8° in closed clusters of uranyl peroxide hydroxide polyhedra.

This study provides structural evidence for an inherently bent $U-O_2-U$ dihedral angle. The persistence of this structural feature suggests a covalent interaction between the peroxide group and the uranyl ion. Such an interaction is unusual, as typically the interaction between uranyl ions and equatorial oxyanions is thought to be almost entirely ionic. In the case of peroxide, covalent interactions with the uranyl ion may significantly alter the properties and even the reactivity of the uranyl ion. The search for other interactions with uranyl ions that provide inherently bent dihedral angles, which provide a driving force for self-assembly into nanoscale clusters, will be aided by a detailed understanding of the electronic aspects of the interactions derived from high-level computational studies.

Acknowledgment. This research was supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy, Grant No. DE-FG02-07ER15880.

Supporting Information Available: Crystallographic data for all compounds and experimental methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA907837U