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Crown and Bowl-Shaped Clusters of Uranyl Polyhedra

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Bowl (U_{16}) and crown-shaped clusters (U_{20R} and U_{24R}) containing 16, 20, and 24 uranyl peroxide polyhedra self-assemble in alkaline aqueous solution under ambient conditions. Structural analyses of crystallized clusters provided details of their topologies. Each contains uranyl hexagonal bipyramids in which two cis edges are peroxide, with a third edge defined by two OH groups, as well as hexagonal bipyramids in which three edges are peroxide. These are the first open uranyl peroxide clusters reported, and they join a growing family of complex cluster topologies based on uranium that hold promise for nanoscale control of chemistry in nuclear energy cycles.

The solid-state structural chemistry of the uranyl ion in inorganic systems has been extensively studied,[1] but it is only within the past few years that nanoscale clusters[2−4] and tubules[5] containing the uranyl ion have been reported. Uranium has been incorporated into several polyoxometalates as an addenda element,[6−11] and recently a cluster of four uranyl peroxide polyhedra was incorporated into an interesting polyoxometalate cluster.[12] Clusters consisting predominantly of uranyl polyhedra with several different topologies containing 24, 28, 32,[2] 40, 50,[3] 36, 44, and 60[4] uranyl polyhedra were reported by us previously. Several of these adopt fullerene topologies.[3,4] These clusters are actinide-based polyoxometalates and hold promise for nanoscale control of reactions of actinides and for a wide range of applications in the nuclear energy cycle.

Three new clusters of uranyl peroxide polyhedra have been obtained by combining uranyl nitrate with peroxide in basic aqueous solutions under ambient conditions.[13] The clusters were crystallized, and their structures were revealed by X-ray diffraction.[14] Unlike clusters that we reported earlier, these are open, forming in one case a bowl-like topology with 16 uranyl polyhedra (U_{16}) and in two cases cyclic ring topologies with crownlike shapes consisting of 20 and 24 uranyl polyhedra (U_{20R} and U_{24R}).

U_{16} consists of 16 uranyl hexagonal bipyramids (Figure 1a, b); eight contain two peroxide equatorial edges in a cis arrangement and two hydroxyl groups (U3 and U4), and eight have three peroxide equatorial edges (U1 and U2). The

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(13) **Synthesis of U_{16}.** Method 1: A total of 1.00 mL of 0.5 M uranyl nitrate hexahydrate in water, 1.00 mL of 30% H_2O_2, 0.80 mL of 4 M NaOH in water, and 0.020 mL of 2 M CsOH in water were combined in a 20 mL scintillation vial. The solution evaporated slowly in air until crystals appeared in solution, and then the vial was capped. Method 2: A total of 1.00 mL of 0.5 M uranyl nitrate hexahydrate in water, 1.00 mL of 30% H_2O_2, 0.80 mL of 4 M NaOH in water, and 0.10 mL of 2 M CsOH in water were combined in a 20 mL scintillation vial. The solution was left open to air until crystals formed, after which the vial was capped. **Synthesis of U_{20R}.** A total of 1.00 mL of 30% H_2O_2 was combined with 1.25 mL of 5 M KOH in water in a 20 mL scintillation vial. A total of 1.00 mL of a 0.5 M uranyl nitrate hexahydrate solution in water was added dropwise, resulting in a solution with pH 13. The solution was left standing in air until crystals had formed several weeks later. **Synthesis of U_{24R}.** A total of 1.00 mL of a 0.5 M solution of uranyl nitrate hexahydrate in water, 1 mL of 30% H_2O_2, 0.80 mL of 4 M NaOH in water, and 0.025 mL of 2 M CsOH in water were combined in a 20 mL scintillation vial. The vial was capped once crystals appeared after several days.

(14) Crystals immersed in oil were placed on cryoloops and cooled in a stream of nitrogen gas to 120 K. A sphere of three-dimensional single-crystal X-ray diffraction data was collected for each using a Bruker Platform gomiometer, an APEX CCD-based detector, and Mo Kα radiation. Data were integrated and corrected for background, Lorentz, and polarization effects using the APEX II. *SADABS* was used to apply corrections for absorption. Structure solutions and refinements were done using *SHELXTL*. Final refinement cycles on the basis of F^2 included all atomic positional coordinates, anisotropic displacement parameters for U sites, and a mixture of anisotropic and isotropic displacement parameters for the remaining atoms. U_{16}: $P4/mnc$, $a = 20.547(1)$ Å, $c = 40.710(3)$ Å, R1 = 5.60, wR2 = 16.50, $S = 0.91$. U_{20R}: $C2/c$, $a = 36.346(2)$ Å, $b = 16.963(1)$ Å, $c = 37.788(2)$ Å, $\beta = 114.167(1)°$, R1 = 6.44, wR2 = 19.16, $S = 0.97$. U_{24R}: $P2_1/c$, $a = 20.369(6)$ Å, $b = 19.760(6)$ Å, $c = 32.864(7)$ Å, $\beta = 124.98(1)°$, R1 = 7.04, wR2 = 18.35, $S = 0.73$.

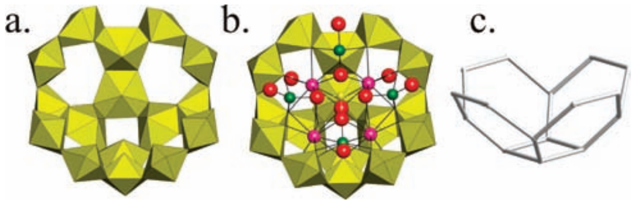

Figure 1. Polyhedral (a) and mixed polyhedral and ball-and-stick (b) representations of U_{16}. The connectivity of the cluster, where solid lines represent shared polyhedral edges, is given in part c. Uranyl polyhedra are yellow, and O, Na, and Cs atoms are red, green, and pink, respectively.

geometries of the uranyl polyhedra are within the error of average bond lengths in well-refined structures,[15] with uranyl ion bond lengths ranging from 1.78(1) to 1.82(2) Å, those from U^{6+} to peroxide O atoms from 2.23(1) to 2.40(1) Å, and those from U^{6+} to hydroxyl O atoms from 2.37(1) to 2.42(1) Å.

U_{16} is bowl-shaped, with four U3 diperoxide hexagonal bipyramids forming the base consisting of a four-membered ring by sharing peroxide edges. Each U3 polyhedron shares a third edge, defined by two hydroxyl groups, with a U4 bipyramid. U4 bipyramids share their peroxide edges with U1 and U2 bipyramids, and these U1 and U2 bipyramids share another peroxide edge with each other. The third peroxide edge of the U1 and U2 bipyramids is unshared. The cluster contains one topological square and four hexagons (Figure 1c).

Four Cs atoms (Cs1) and four Na atoms (Na2) are located within the bowl of U_{16} (Figure 1b). Cs1 atoms are coordinated by nine O atoms, including a H_2O group located at about the center of the hexagon in the topology. Na2 atoms are coordinate by five O atoms, including three O atoms of uranyl ions. The U5 cation is located on the 4-fold rotational axis within the bowl of U_{16}, at about the same level as the Na atoms. It is coordinated by four symmetrically identical and virtually coplanar O24 atoms at 2.05(2) Å, as well as one O23 atom, which is also located on the 4-fold axis toward the core of the cluster, at a distance of 2.26(3) Å. This is a highly unusual coordination geometry about U^{6+}, although some structures contain U^{6+} in distorted octahedral environments with similar bond lengths.[15] The displacement parameters for U5, O23, and O24 are large, and the observed coordination geometry likely is an average of less symmetric configurations.

The walls of U_{16} have composition $[(UO_2)_{16}(O_2)_{24}(OH)_8]^{24-}$. Including the interior components gives composition $UO_4Na_4Cs_4(H_2O)_9[(UO_2)_{16}(O_2)_{24}(OH)_8]^{14-}$. The regions between the U_{16} clusters contain numerous Na and H_2O sites that exhibit disorder.

U_{20R} contains 16 hexagonal bipyramids containing two peroxide equatorial edges in a cis arrangement and two hydroxyl groups, and four that contain three peroxide equatorial edges (Figure 2). Refined uranyl ion bond lengths range from 1.78(1) to 1.84(1) Å, bonds from U^{6+} to O atoms of peroxide range from 2.26(2) to 2.41(2) Å, and those to O atoms of hydroxyl groups range from 2.32(1) to 2.43(2) Å.

Diperoxide uranyl hexagonal bipyramids share OH−OH edges, forming dimers of composition $(UO_2)_2(O_2)_4(OH)_2{}^{2-}$, with eight of these dimers occurring in U_{20R}. These dimers are each linked to two other compositionally identical dimers by sharing one peroxide edge of each polyhedron, resulting in a ring of 16 polyhedra. The ring structure is reinforced by four triperoxide polyhedra that share two of their edges with bipyramids of two different dimers. The result is a complex cyclic crownlike structure consisting of 20 polyhedra (Figure 2).

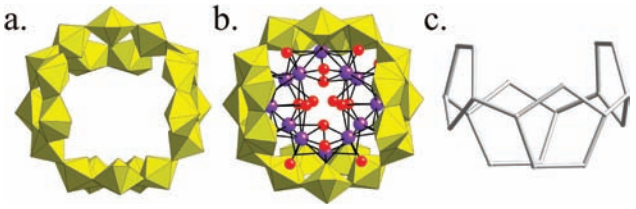

Figure 2. Polyhedral (a) and mixed polyhedral and ball-and-stick (b) representations of U_{20R}. The connectivity of the cluster, where solid lines represent shared polyhedral edges, is given in part c. Uranyl polyhedra are yellow, and O and K atoms are red and purple, respectively.

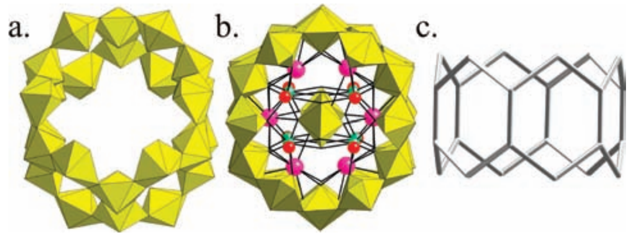

Figure 3. Polyhedral (a) and mixed polyhedral and ball-and-stick (b) representations of U_{24R}. The connectivity of the cluster, where solid lines represent shared polyhedral edges, is given in part c. Uranyl polyhedra are yellow, and O, Na, and Cs atoms are red, green, and pink, respectively.

The topology of U_{20R} consists of four pentagons (Figure 2c). None share edges but rather are linked by single connections through the sharing of edges of polyhedra.

The U11 cation is located at the center of U_{20R} as a uranyl triperoxide hexagonal bipyramid. U_{20R} contains 12 K atoms populating six symmetrically distinct sites. They are bonded to O atoms of uranyl ions of both the U_{20R} crown and the U11 position at the center of the cluster. They also include H_2O groups in their coordination spheres that are not bonded to U^{6+}.

The crown of U_{20R} has composition $[(UO_2)_{20}(OH)_{16}(O_2)_{28}]^{32-}$. Including the inner constituents gives a composition of $K_{12}(H_2O)_{10}(UO_2)(O_2)_3[(UO_2)_{20}(OH)_{16}(O_2)_{28}]^{24-}$. The X-ray data revealed disordered K and H_2O sites outside the clusters.

U_{24R} contains 12 uranyl hexagonal bipyramids with two peroxide equatorial edges and two hydroxyl groups defining a third edge and 12 uranyl triperoxide hexagonal bipyramids. The polyhedral geometries of U_{24R} are within typical ranges. The uranyl ion bond lengths range from 1.76(3) to 1.88(3) Å, bonds from U^{6+} to O atoms of peroxide range from 2.22(4) to 2.46(3) Å, and those to O atoms of hydroxyl groups range from 2.33(3) to 2.42(3) Å.

In U_{24R}, diperoxide uranyl polyhedra share edges defined by hydroxyl groups, forming dimers of composition $(UO_2)_2(O_2)_4(OH)_2{}^{2-}$ (Figure 3). These dimers are arranged such that the hydroxyl edges define a plane that bisects the cluster. The dimers are equally spaced about the circumference of the cluster and are linked on either side by sharing peroxide edges with triperoxide uranyl polyhedra. The topo-

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logy consists of hexagons, with each hexagon sharing trans edges with two others, forming a ring of six hexagons.

U_{24R} encompasses four Cs atoms, eight Na atoms, and two uranyl ions. The Cs atoms are located adjacent to hexagons of the cluster topology, where they are bonded to uranyl ion O atoms and equatorial ligands of the cluster and to ligands of the two uranyl ions that are located inside the cluster. The Na cations are each bonded to three O atoms of uranyl ions that are in the cluster walls, as well as ligands of the uranyl ions located inside the cluster, and a single H_2O group in each case. Two U13 uranyl ions are located along the central axis of the cluster. Their coordination polyhedra are distorted and probably reflect some positional disorder but appear to form a dimer of composition $(UO_2)_2(O_3)_5$. The U_{24R} crown has composition $[(UO_2)_{24}(O_2)_{36}(OH)_{12}]^{36-}$. Including the interior constituents, the composition is $Cs_4Na_8(UO_2)_2(O_2)_5[(UO_2)_{24}(O_2)_{36}(OH)_{12}]^{30-}$.

U_{16} is the first bowl-shaped uranyl peroxide cluster. It is topologically related to the U_{24} cluster that we reported earlier.[2] U_{24} consists only of uranyl hexagonal bipyramids with two peroxide edges in a cis configuration and another equatorial edge defined by two hydroxyl groups. These polyhedra share peroxide equatorial edges, forming tetramers of polyhedra that are analogous to that at the base of U_{16}. The linkages of this tetramer to four other bipyramids by sharing hydroxyl−hydroxyl edges also occur in both clusters. The tops of U_{16} are terminated by triperoxide bipyramids, which are not present in U_{24}.

The closed cluster U_{24} formed with Li as the only counterion, whereas U_{16} contains both Cs and Na. Because Cs is much larger than Li, this suggests that U_{16} is held open by Cs atoms, preventing the curvature required for closure of the cluster. The longest distances between U atoms near the lips of the U_{16} bowl, of which there are four symmetrically identical distances, are 14.10 Å. The equivalent distances in the U_{24} cluster, which is a closed sphere, range from 12.87 to 12.94 Å, consistent with Cs atoms propping U_{16} open.

The U_{20R} topology, containing four pentagons linked into a ring, can be extracted from the larger closed U_{28} cluster.[2] In U_{28}, all of the polyhedra are uranyl triperoxide hexagonal bipyramids, whereas U_{20R} has uranyl polyhedra with two and three peroxide edges.

The U_{24R} topology is rather unique in that it contains only hexagons, all hexagons shared edges with two adjacent hexagons, and the overall cluster consists of a six-membered ring of edge-sharing hexagons. None of the topologies we have reported earlier for uranyl peroxide clusters are closely related to this unusual arrangement.

Those clusters with 24, 28, 32,[2] 40, 50,[3] 44, and 60[4] uranyl polyhedra contain either all uranyl diperoxide hydroxide polyhedra or uranyl triperoxide polyhedra, whereas only that containing 36 has both types of polyhedra.[4] In contrast, all three clusters reported here have mixtures of these two types of polyhedra, with U_{16} and U_{24R} containing equal proportions and U_{20R} containing only four uranyl triperoxide polyhedra. This suggests that open clusters can be encouraged by tuning synthesis conditions to include both of these polyhedra types in the precursor aqueous solution. There is currently little information concerning the speciation in uranyl solutions with abundant peroxide,[16] and studies of such will be hampered by the rapid formation of extended clusters.

There is a large body of literature that examines the synthesis, structures, and properties of polyoxometalates, especially those containing W, Mo, and P.[17] Relatively early in polyoxometalate modern chemistry, the $[H_7P_8W_{48}O_{184}]^{33-}$ polyoxoanion was isolated.[18] This has proven to be an important anion that has served as a means of controlling the nucleation of interesting metal cores.[19−22] The appearance and dimensions of the U_{24R} cluster reported herein have commonalities with the $[H_7P_8W_{48}O_{184}]^{33-}$ polyoxoanion. As measured from the centers of O atoms that define the edges of the interior of the clusters, the distance is 10.0 and 9.0 Å for U_{24R} and $[H_7P_8W_{48}O_{184}]^{33-}$, respectively. The outer bounds of the clusters, as measured from the centers of O atoms, are 19.3 and 22.3 Å for U_{24R} and $[H_7P_8W_{48}O_{184}]^{33-}$, respectively. Compositionally, of course, these two clusters have little in common. Clusters such as U_{16}, U_{20R}, and U_{24R} may also prove useful in directing chemistry at the nanoscale.

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Supporting Information Available: Crystallographic CIF file for U_{16}, U_{20R}, and U_{24R} and IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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