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VIP Polyoxometalates

Hybrid Uranium–Oxalate Fullerene Topology Cage Clusters**

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Polyoxometalates have been intensely studied owing to useful properties with broad applications.[1] Polyoxometalates have been reported that are decorated by attached organic molecules, and also that have specific polyoxometalate clusters linked through organic moieties, but none have integral organic molecules that bridge metal oxide polyhedra within the polyoxometalate itself. Nanoscale magnet clusters with integral organic molecules that bridge metal oxide polyhedra are known,[2–6] suggesting extension of integral organic linkages to polyoxometalates. Creation of such polyoxometalates may enhance the possibility of tuning aqueous solubility and response to externally applied radiation fields or oxidizing conditions. Here we extend the complex family of nanoscale clusters of uranyl peroxide polyhedra by incorporating oxalate bridges.

Emphasizing development of nanoscale control of actinide materials, we have reported the synthesis and structural topologies of sixteen complex clusters of uranyl peroxide bipyramids that contain as many as sixty uranium atoms.[7–12] In these bipyramids, uranyl ions are coordinated by two or three peroxide groups arranged such that the apices of the bipyramid correspond to oxygen atoms of the uranyl ion, and peroxide groups define two or three equatorial edges of the bipyramid. These hexagonal bipyramids are linked through the sharing of equatorial edges, with a shared edge corresponding either to a single peroxide group or to two hydroxy groups. These cage-, crown-, and bowl-shaped clusters are a major departure from the infinite sheets of uranyl polyhedra that typically occur in extended solids. Our experimental evidence indicates the curvature in these clusters is caused by the uranyl-peroxide-uranyl bridge that is inherently bent.[9] We hypothesized that the curvature inherent in a ring of four, five, or six edge-sharing bipyramids containing uranyl ions and peroxide groups could be used, in combination with appropriate organic molecules, to create nanoscale inorganic–organic hybrid cage clusters. Here we report the synthesis of two uranyl-oxalate cage clusters designated $U_{60}Ox_{30}$ and $U_{36}Ox_{6}$ that form in an aqueous mixture of uranyl nitrate, hydrogen peroxide, and oxalic acid under ambient conditions.

The cage clusters $U_{60}Ox_{30}$ and $U_{36}Ox_{6}$ self-assemble in aqueous solution under ambient conditions, as shown by small-angle X-ray scattering data collected from solutions that had been in contact with growing crystals. Addition of counterions such as K^+ induces these negatively charged clusters to precipitate into crystals suitable for structure analysis using X-ray diffraction (Figure 1). The largest of these, $U_{60}Ox_{30}$, contains sixty uranium cations, each of which is present as an approximately linear uranyl ion $(UO_2)^{2+}$ with U−O bond lengths in the range 1.73(1) to 1.85(2) Å. The uranyl ions are approximately perpendicular to the cluster walls, and are coordinated by two peroxide groups arranged at the equatorial edges of hexagonal bipyramids with U−O bond lengths in the range 2.26(1) to 2.38(1) Å, with two additional O atoms in each polyhedron corresponding to an oxalate group with U−O bond lengths ranging from 2.41(1) to 2.53(1) Å. Peroxide O−O bond lengths range from 1.43(2) to 1.55(2) Å. The coordination environment about a single U cation is shown in Figure 2. The overall cluster has composition $[\{(UO_2)(O_2)\}_{60}(C_2O_4)_{30}]^{60-}$ and the charge is balanced by K cations located within and between the cage cluster. Each uranyl polyhedron shares the two equatorial edges defined by peroxide groups with adjacent uranyl polyhedra, with five such polyhedra forming a ring of polyhedra. These rings of uranyl polyhedra are linked into clusters through bidentate oxalate groups that bridge between two different bipyramids, each of which is in a different ring of bipyramids.

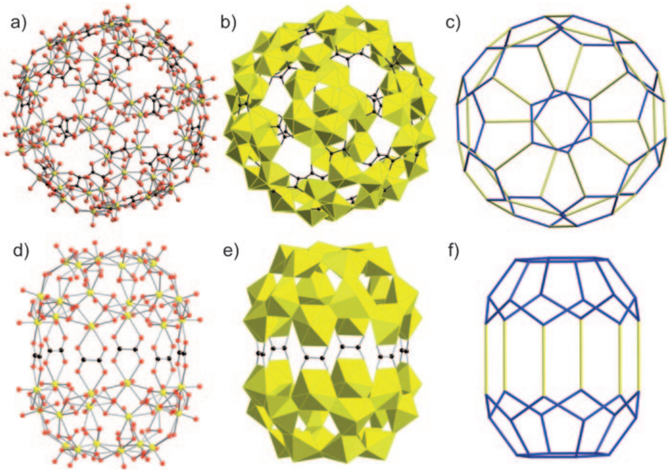

Figure 1. Ball-and-stick, polyhedral, and graphical representations of the $U_{60}Ox_{30}$ (a,b,c) and $U_{36}Ox_{6}$ (d,e,f) clusters. U atoms and polyhedra are shown in yellow, O atoms in red, and C atoms in black. The vertices of the graphical representations (c,f) correspond to U atoms and lines represent connections between U atoms, with blue corresponding to shared polyhedral edges between uranyl bipyramids and yellow to bridges through oxalate.

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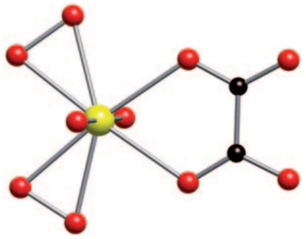

Figure 2. Ball-and-stick representation of the coordination environment about U^{6+} ions in $U_{60}Ox_{60}$. U, O, and C are represented by yellow, red, and black spheres, respectively. The uranyl ion is oriented roughly perpendicular to the plane of projection, the peroxide groups are on the left, and the oxalate group is to the right.

Linkage of rings of uranyl polyhedra through oxalate ligands in $U_{60}Ox_{30}$ gives a spherical cage cluster consisting of 60 uranyl hexagonal bipyramids and 30 oxalate units (Figure 1 a,b). A graphical representation of the cluster topology is shown in Figure 1 c. Vertices within the graph correspond to U atoms, and lines extending between the vertices denote shared polyhedral elements. Blue lines correspond to shared edges between uranyl bipyramids, whereas yellow lines indicate uranyl bipyramids that are bridged through an oxalate group. The graph consists of pentagons, defined by the edge-sharing uranyl hexagonal bipyramids, and hexagons consisting of connections corresponding to three bipyramids and three oxalate units. This is a fullerene topology containing 12 isolated pentagons as well as 20 hexagons. It is topologically identical to C_{60} buckminsterfullerene and the U_{60} cluster we reported earlier than contains only uranyl hexagonal bipyramids.[10] There are 1812 fullerene topologies that contain 60 vertices, and the isomer adopted by $U_{60}Ox_{30}$ has the highest ideal symmetry and is the only one that has no adjacent pentagons.[13]

The cluster $U_{36}Ox_{6}$ contains 36 uranyl ions with U−O bond lengths in the range 1.764(9) to 1.817(7) Å. Unlike $U_{60}Ox_{30}$, this cluster contains two compositionally distinct types of uranyl polyhedra. There are 24 uranyl ions that are each coordinated by three bidentate peroxide groups arranged along three equatorial edges of hexagonal bipyramids capped by the uranyl ion O atoms. The remaining 12 uranyl ions are each linked to two bidentate peroxide groups, and one bidentate oxalate group completes the hexagonal bipyramidal coordination. The $U{-}O_{peroxo}$ and $U{-}O_{oxalate}$ bond lengths range from 2.326(6) to 2.385(6) and 2.468(6) to 2.481(6) Å, respectively. The peroxide O−O distances range from 1.482(9) to 1.524(8) Å. The resulting cluster, shown graphically in Figure 1 f, is an oblate spheroid with uranyl-polyhedral oxalate bridges located only in the equatorial plane (Figure 1 d,e). The composition of the cage cluster is $[(UO_2)_{36}(O_2)_{48}(C_2O_4)_6]^{36-}$ and the charge is balanced by K cations located inside and between the clusters. Both ends of the spheroid are defined by topological hexagons consisting of peroxide-edge sharing uranyl triperoxide polyhedra. These bipyramids share peroxide edges with 12 additional bipyramids, giving six topological pentagons. Linkages between the two uranyl-bipyramidal halves of the cluster are through the six bridging oxalate units. The graphical representation (Figure 1 f) reveals that the oxalate linkages, together with the bipyramids, define six topological hexagons. The overall cluster is a fullerene topology with twelve pentagons and eight hexagons, a topology that has also been found constructed only of uranyl hexagonal bipyramids in the case of U_{36}.[10]

Oxalate ligands are ideal for bridging between uranyl hexagonal bipyramids because the bonding requirements of the O atoms are a good match with the bonding requirements of the uranyl ion, and the ligand is geometrically compatible with forming an edge of the bipyramid. We earlier reported crystallization of clusters that contain five uranyl hexagonal bipyramids analogous to those shown in Figure 2. In these, peroxide groups correspond to the edges that are shared between the bipyramids, with an additional unshared edge being an oxalate ligand.[9] However, these clusters did not link into cage clusters, although they were crystallized under conditions that are similar to those of the current study. The differentiating synthesis parameter is the uranium/oxalate ratio: less oxalate favors assembly of larger clusters.

The clusters $U_{60}Ox_{30}$ and $U_{36}Ox_{6}$ are topologically derived from those that contain only uranyl polyhedra by replacing shared edges defined by two hydroxy groups by the oxalate group. This has a significant impact on the size of the cluster, as well as the dimensions of the void spaces within the cluster walls. The total diameter, extending to the edges of the bounding O atoms, is 27.0 and 31.0 Å for the U_{60} and $U_{60}Ox_{30}$ clusters, respectively. More significant is the change in size of the topological hexagons in the clusters. These correspond to six uranyl hexagonal bipyramids in U_{60} that are linked by the sharing of alternating peroxide and hydroxide edges, but in $U_{60}Ox_{30}$ these rings have oxalate bridges instead of the shared hydroxide edges (Figure 3). As a result, the diameter of the void space within the ring is increased by 2 Å by incorporation of oxalate.

Crystals containing $U_{60}Ox_{30}$ were isolated from their mother solution, dried, and subsequently re-dissolved in ultrapure water. Small angle X-ray scattering (SAXS) data collected for the resulting solution indicated the presence of a monodisperse cluster (Figure 4). The scattering data was modeled as a spherical shell, which gave an inner and outer radius of 5.1 and 15.6 Å, respectively. These values compare well with those derived from the crystallographic data, which gave a cluster radius of 15.5 Å as measured from the edges of the bounding O atoms. The SAXS data show that clusters of

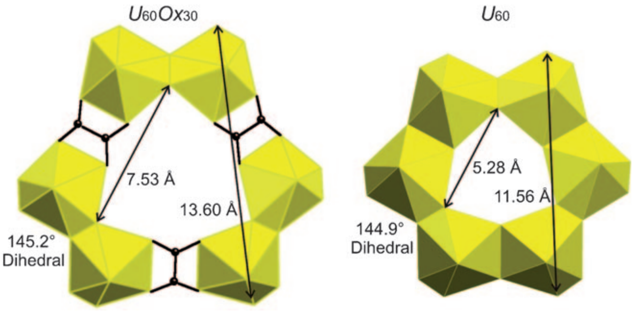

Figure 3. Comparison of structural fragments from the $U_{60}Ox_{30}$ and U_{60} clusters. These fragments correspond to topological hexagons. Uranyl polyhedra are shown in yellow and C atoms are colored black. Geometric parameters shown are from the crystal structure determinations.

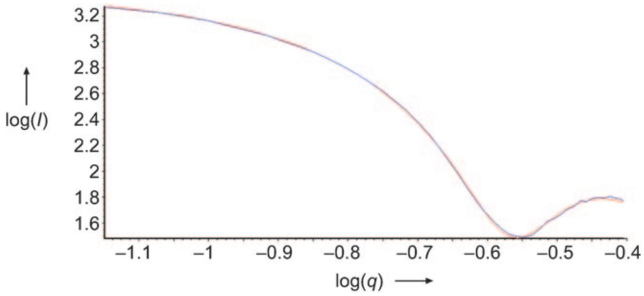

Figure 4. Small-angle X-ray scattering data (blue line) and model fit (red line) for ultrapure water containing dissolved $U_{60}Ox_{30}$ clusters. The data is modeled as a spherical shell with inner and outer radii of 5.1 and 15.6 Å, respectively.

$U_{60}Ox_{30}$ grown under specialized conditions can be dissolved in ultrapure water, where they remain intact.

The clusters $U_{60}Ox_{30}$ and $U_{36}Ox_{6}$ both adopt fullerene topologies consisting of 12 pentagons and an even number of hexagons. Consistent with our earlier findings for cage clusters containing only uranyl polyhedra,[7–12] both clusters select the isomer (for the given number of vertices) that has the highest ideal symmetry.

Experimental Section

Crystals containing $U_{36}Ox_{6}$ were synthesized by loading aqueous $UO_2(NO_3)\cdot 6H_2O$ (0.5 M, 0.1 mL), H_2O_2 (30%, 0.1 mL), LiOH (2.38 M, 0.1 mL), KCl (0.5 M, 0.05 mL), and $H_2C_2O_4$ (0.5 M, 0.15 mL) in a 2 mL scintillation vial. The initial pH of the mixed solution was 4.3. Yellow blocks containing $U_{36}Ox_{6}$ crystallized within a week during solution evaporation under ambient conditions.

Crystals containing $U_{60}Ox_{30}$ were synthesized by loading aqueous $UO_2(NO_3)\cdot 6H_2O$ (0.5 M, 0.1 mL), H_2O_2 (30%, 0.1 mL), tetramethylammonium hydroxide (25%, 0.1 mL), $K_2S_2O_7$ (0.25 M, 0.125 mL), and $H_2C_2O_4$ (0.5 M, 0.1 mL) in a 2 mL scintillation vial. The initial pH of the solution as mixed was 5.8. Yellow blocks containing $U_{60}Ox_{30}$ crystallized within two weeks under ambient conditions. Crystals of $U_{36}Ox_{6}$ and $U_{60}Ox_{30}$ were grown solely to provide an ordered array of clusters suitable for single-crystal X-ray diffraction structure analyses. Crystals were harvested from their mother solutions as soon as they had grown large enough for diffraction experiments. In the case of $U_{36}Ox_{6}$, the crystals were invariably small and difficult to harvest. Larger crystals of $U_{60}Ox_{30}$ were obtained, and these were harvested for subsequent spectroscopic and elemental analysis.

Crystals of $U_{60}Ox_{30}$ were washed lightly with deionized water under vacuum and were subsequently dissolved for analysis using a Perkin–Elmer ICP-OES. Analysis for three separately washed samples gave U/K ratios of 1:0.97, 1:0.99, and 1:0.98, consistent with the formula $K_{60}[\{(UO_2)(O_2)\}_{60}(C_2O_4)_{30}]\cdot n\,H_2O$. Thermogravimetric analysis for crystals of $U_{60}Ox_{30}$ (see the Supporting Information) revealed a series of weight losses extending from about 60 to 500 °C that total approximately 28%.

Each cluster was crystallized to permit X-ray diffraction analysis of the structure of the cluster. Structure determinations for such materials are challenging because of the contrast between uranium and the lighter elements present, the presence of void spaces in the crystals, and disorder of counter ions and H_2O inside the clusters. However, details of the structural connectivities of the uranyl-based clusters are attainable through X-ray diffraction.[7–12]

Crystals were placed on cryo-loops in oil and cooled to 110 K for data collections using a Bruker APEX diffractometer equipped with monochromated $Mo_{K\alpha}$ radiation. A sphere of data was collected for each crystal using framewidths of 0.3° in ω. Data were corrected for Lorentz, polarization, and background effects using the Bruker APEXII software, and empirical corrections for absorption were performed using SADABS. Structure solutions and refinements were done with SHELXTL.[14] The data were corrected for solvent-accessible void space using SQUEEZE as implemented in PLATON.[15] Crystallographic parameters and refinement details are provided in the Supporting Information. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-421994 ($U_{36}Ox_{6}$) and CSD-421993 ($U_{60}Ox_{30}$).

SAXS data were collected using a Bruker Nanostar equipped with a Cu microfocus source, Montel multilayer optics, and a HI-STAR multiwire detector. Data were collected with a sample-to-detector distance of about 25.5 or 65.5 cm with the sample chamber under vacuum. Solutions were placed in 0.5 mm diameter glass capillaries with the ends of the capillary sealed using wax. Ultrapure water was placed in an identical capillary for background measurement. Scattering data were collected for the mother solution standing over crystals of $U_{60}Ox_{30}$ as well as for water in which selected crystals of $U_{60}Ox_{30}$ had been dissolved.

Infrared spectra collected for single crystals containing $U_{60}Ox_{30}$ and $U_{36}Ox_{6}$ using a diamond attenuated total reflectance objective readily confirmed the presence of oxalate, uranyl ions, and H_2O groups. The spectra are provided in the Supporting Information. UV/Vis spectra were collected for crystals of $U_{60}Ox_{30}$ and $U_{36}Ox_{6}$ using a Craig Instruments spectrometer and are included in the Supporting Information.

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