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VIP Polyoxometalates

Symmetry versus Minimal Pentagonal Adjacencies in Uranium-Based Polyoxometalate Fullerene Topologies**

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Polyoxometalates are centuries old,[1] and Keggin established the first structure of a heteropolyoxometalate compound in 1933.[2] Actinides have recently been incorporated into polyoxometalates of transition metals,[3–7] but only three studies report actinide-based polyoxometalate clusters.[8–10] Yet actinides are ideal candidates for self-assembly into clusters that may possess interesting properties associated with the complexity of the f electrons, and such clusters could be useful in the nuclear fuel cycle. Duval et al.[9] reported a cluster with a polyoxometalate core containing six uranium atoms, and we recently described clusters of uranyl peroxide hydroxide isopolyhedra, consisting of 24, 28, 32,[8] 40, and 50[10] polyhedra. Uranyl peroxide clusters self-assemble in alkaline solutions under ambient conditions and provide a glimpse into a potentially large and complex family of polyoxometalates.

Clusters with fullerene topologies such as C_{60} exhibit striking symmetric beauty and important properties.[11] Fullerenes consist of 12 topological pentagons and at least two hexagons. Topological pentagons placed in a sheet of hexagons create curvature, with twelve such units required to close the topology into a cluster.[12] Over the past decade, analogues of C_{60} fullerene have been postulated, such as fullerene-like molecules of silicon atoms and mixtures of Group 13 and Group 15 elements, although confirmation by experiment is lacking.[13–15] Several inorganic fullerene-like cages have been synthesized using solid-state techniques. Zintl phases have produced a C_{60}-like moiety in $In_{48}Na_{12}$,[16] and transition-metal phases with spherical fullerene-like molecules have been synthesized using iron and copper.[17] Superfullerene species have been reported that contain 132 molybdenum atoms.[18]

Curvature in a fullerene structure relates to the distribution of pentagons in its topology.[12] Adjacent pentagons increase local curvature. For carbon, increased curvature results in strain by decreasing orbital overlap.[12] No fullerene topology exists without adjacent pentagons and with less than 60 vertices. Only one fullerene structure with 60 vertices and no adjacent pentagons is possible, and it is adopted by C_{60} because it results in the most favorable orbital overlap. In carbon fullerenes with less than 60 vertices, those with the minimum number of adjacent pentagons are expected to be the most stable.[19]

The emerging structural complexities of uranyl peroxide clusters suggest the possibility of creating large fullerene-topology clusters with high stability. This prospect provides the impetus for a combinatorial approach to exploring the uranyl peroxide system. Subtle changes in growth conditions are known to result in different structures in this system.[8,10]

Clusters of composition $[UO_2(O_2)(OH)]_{60}^{60-}$ (U60) formed when uranyl nitrate, hydrogen peroxide, potassium chloride, and lithium hydroxide were combined in aqueous solution at pH 9.0. Well-faceted millimeter-sized crystals with approximate composition $Li_{48+m}K_{12}(OH)_m[UO_2(O_2)(OH)]_{60}(H_2O)_n$ ($m \approx 20$ and $n \approx 310$, see the Supporting Information) containing these clusters formed within seven days. Single-crystal X-ray diffraction gave the cubic space group $Fm\bar{3}$ and resolved the atomic positions of the uranyl peroxide polyhedra and potassium cations. The cluster is nearly spherical, with an outer diameter of 24.3 Å, measured from the centers of oxygen atoms on either side (Figure 1 a).

U60 consists of sixty compositionally identical uranyl peroxide hydroxide polyhedra (Figure 1 a–c). Each has an

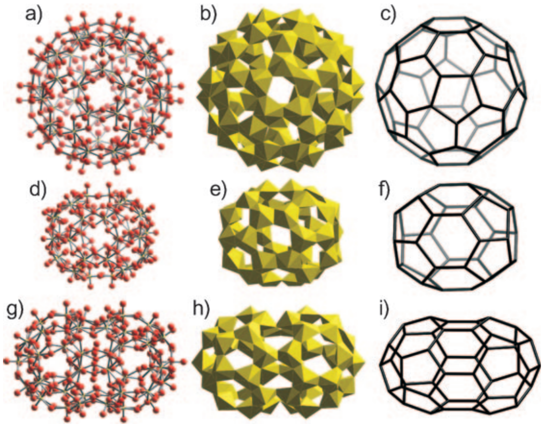

Figure 1. Representations of the uranyl peroxide components of the structures of U60 (a–c), U36 (d–f), and U44 (g–i). Ball-and-stick (left) and polyhedral (center) representations are complemented by graphs showing the cluster topologies (right).

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approximately linear $(UO_2)^{2+}$ uranyl ion that is coordinated by two peroxide groups positioned along equatorial edges of a hexagonal bipyramid and by two hydroxy groups that define a third edge of the bipyramid. These polyhedra are linked by shared edges defined by the two peroxide groups and the edge formed by the two hydroxy groups. A graph representing U60 is shown in Figure 1c, where vertices represent uranyl polyhedra and lines connecting vertices correspond to shared edges between polyhedra. There are 60 vertices, 12 pentagons, and 20 hexagons that form an exact truncated icosahedron. The structure of U60 is topologically identical to C_{60}.

Synthesis of U60 clusters was readily repeated, but omission of either lithium or potassium from the aqueous solution, or performing the reaction at $pH > 9$, yielded clusters with different (smaller) topologies, or no crystals suitable for X-ray diffraction were recovered. The crystallographic data indicate that potassium ions are located inside the U60 cluster, adjacent to pentagons in the structure.

The uranyl peroxide portion of the U60 cluster has a net charge of -60. Within the bond-valence formalism,[20,21] the uranyl peroxide portion of the cluster should form bonds extending to other parts of the structure totaling one valence unit per polyhedron. The oxygen atoms of the uranyl ions may form bonds totaling as much as 0.5 valence units each, and their orientation indicates that half of this bond valence will be distributed to constituents inside the cluster, and the remainder will be incident upon constituents outside the cluster. Hydrogen bonds associated with the sixty hydroxy groups in the polyhedra may extend to anions either inside or outside the cluster.

Sixty oxygen atoms of uranyl ions (O_{Ur}) occur on the inside of the U60 cluster, where each is bonded to one potassium cation with a bond strength of roughly 0.2 valence units. The potassium cations are located below the centers of the pentagons in the cluster topology and are bonded to five oxygen atoms of uranyl ions, giving a pyramidal coordination with bond lengths ranging from 2.84(2) to 2.87(2) Å. Difference Fourier maps revealed electron density both inside the cluster and between adjacent clusters at a level consistent with disordered oxygen and lithium atoms. The most likely location of lithium cations within the cluster is below the hexagonal rings of the topology, where they would bridge between two O_{Ur} anions that belong to adjacent uranyl ions in the ring and would bond to two H_2O groups located inside the U60 cluster, resulting in a tetrahedral coordination environment about the lithium cations (Figure 2). It is unlikely that more than one lithium cation will bond to any given O_{Ur} atom, as together with the existing bond to a potassium cation, this would result in overbonding. As many as three lithium cations could occur associated with a hexagon in the topology, but in this case sites in adjacent hexagons would have no associated lithium cations. Lithium cations associated with a given hexagon in the topology could be present in different configurations. These observations may explain the disorder of the electron density within the cluster, and available sites could accommodate as many as 30 lithium cations. Together with the potassium cations, as many as 42 positive charges could occur within the cluster, thus reducing the net charge of the cluster to -18, which must then be balanced by cations located outside the clusters.

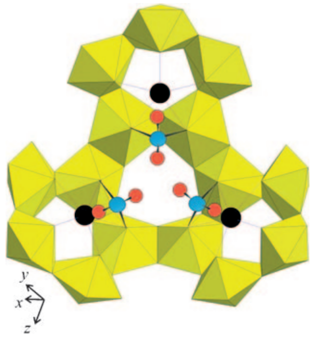

Figure 2. Possible lithium positions in U60. K black, Li blue, H_2O red.

Clusters of composition $[(UO_2)_{36}(O_2)_{41}(OH)_{26}]^{36-}$ were obtained from an aqueous solution of uranyl nitrate, hydrogen peroxide, and lithium hydroxide at $pH \approx 12.5$. The crystals containing these structures have the approximate composition $Li_{36}[(UO_2)_{36}(O_2)_{41}(OH)_{26}](H_2O)_y$ (see the Supporting Information). The clusters consist of 36 uranyl polyhedra (U36), of which ten have composition $(UO_2)(O_2)_3$ and 26 are $(UO_2)(O_2)_2(OH)_2$ (Figure 1 d–f). The fullerene topology contains twelve pentagons and eight hexagons (Figure 1 f). All pentagons in the topology share two of their edges with adjacent pentagons. There are fifteen fullerene isomers with 36 vertices,[12] and the topology adopted by U36 has the fewest pentagonal adjacencies. U36 is notably the first cluster that contains two types of uranyl peroxide polyhedra. It is oblong, with outer diameters of 18.5 and 17.7 Å (length and width), measured from the centers of bounding oxygen atoms.

Clusters containing 44 $(UO_2)(O_2)_3$ polyhedra with composition $[(UO_2)(O_2)_{1.5}]_{44}^{44-}$ (U44) were crystallized from an aqueous solution containing uranyl nitrate, hydrogen peroxide, potassium bisulfate, and sodium hydroxide. Crystals containing these clusters have the approximate composition $(K,Na)_{44}[(UO_2)(O_2)_{1.5}]_{44}(H_2O)_x$ (see the Supporting Information). These peanut-shaped (Figure 1 g–i) fullerene-topology clusters each contain twelve pentagons and twelve hexagons, and they have diameters of 26.8 and 17.8 Å (length and width), measured from the centers of bounding O_{Ur} atoms. There are 89 fullerene topologies containing 44 vertices,[12] and that with the fewest pentagonal adjacencies has eight pentagons that share a single edge with another pentagon and four that share two edges with other pentagons. U44 does not adopt the topology with the fewest pentagonal adjacencies (Figure 1 i). It has D_{3d} symmetry and contains six pentagons that share one of their edges with another pentagon and six that share three of their edges with other pentagons.

The U44 cluster contains partially disordered sites that are occupied by potassium and sodium ions and H_2O. Additional sodium and H_2O sites are located between adjacent clusters. The sodium and potassium cations inside the clusters are below the centers of the pentagons in the topology, where they each link to five O_{Ur} atoms. H_2O molecules are located below the centers of hexagons of the topology, where they are presumably held by hydrogen bonds.

With the report of U36, U44, and U60 clusters, five uranyl peroxide clusters are known to have fullerene topologies. U28, U36, U44, U50, and U60 adopt topologies with ideal symmetries T_d, D_{6h}, D_{3d}, D_{5h}, and O_h, respectively. In the case of carbon, fullerene topologies with no or minimal pentagonal adjacencies are favored, probably because of orbital overlap considerations. In uranyl peroxide fullerenes, the polyhedra are "hinged" by polyhedral edges defined by peroxide or by two hydroxy groups. Interactions between the U^{6+} ion of the uranyl ion and the equatorial peroxide and hydroxy ligands are expected to be mostly ionic; as such, the U-O$_{\text{peroxide}}$-U and U-OH-U bond angles are pliable, and there appears to be no reason based on bonding arguments to expect adjacent pentagons in these topologies to be destabilizing relative to shared edges between hexagons and pentagons.

Cluster symmetry appears to be an important factor in determining the topology of a uranyl peroxide fullerene cluster. Species U28, U36, U50, and U60 all adopt the corresponding fullerene topology with the fewest pentagonal adjacencies, or, in the case of U60, the one of 1812 topologies with no pentagonal adjacencies. This result suggests that pentagonal adjacencies are a factor in uranyl peroxide fullerene topologies. However, in the case of U28, U36, U50, and U60, the topology with the minimum number of pentagonal adjacencies is also that of highest symmetry, and we contend that symmetry is a major factor in determining the relative stability of these clusters. Consistent with this assessment, the 44-vertex fullerene topology with the least number of pentagonal adjacencies does not have the highest symmetry of the 89 possibilities, and it is not adopted by the U44 cluster. The topology with the fewest pentagonal adjacencies has ideal D_2 symmetry. The higher-symmetry topologies with 44 vertices belong to point groups D_{3d} (three), D_{3h} (two), and T (one). Cluster U44 adopts D_{3d} symmetry. The degree of sphericity also appears to be important, as the 44-vertex topology with T symmetry was not adopted by U44, probably owing to its pronounced triangular shape, which results in high curvature in some regions. The importance of symmetry in carbon fullerene-topology clusters was recognized early by Kroto[19] who observed that structural factors should favor the more symmetric isomers. In higher-symmetry clusters, strain is more evenly distributed throughout the cluster. It has been demonstrated that self-assembly of structural units preferentially leads to higher-symmetry products.[22]

In stark contrast to the harsh conditions for synthesis of carbon fullerenes, uranyl peroxide clusters self-assemble in aqueous solutions and persist under ambient conditions. They can be maintained in solution for several months, and they readily crystallize into extended structures. In another departure from carbon-fullerene structures, incorporation of squares in the topologies of uranyl peroxide polyhedra, as observed in U24, U32, and U40,[8,10] presents the possibility of unprecedented topological variability. The chemical behavior of this family of uranyl peroxide clusters is expected to be rather varied and different from typical uranyl aqueous chemistry, and the diversity of accessible structures suggests chemical tuning for specific purposes.

Currently, the details of interactions between the uranyl polyhedra and the counterions remain unclear, but it is evident that manipulation of these counterions results in different cluster topologies. Syntheses with only lithium as a counterion have resulted in U24, U32, and U36, whereas those with potassium only have given U28. A mixture of sodium and potassium provided U44, and lithium and potassium together resulted in U60. Organic cations were used in the synthesis of U40 and U50 together with lithium, although the role of these cations within the clusters is unknown. The pH value of the solution may also be important, with less alkaline solutions appearing to favor larger clusters.

Experimental Section

Cluster Synthesis: U60: Aqueous solutions of uranyl nitrate hexahydrate (0.5 M, 1 mL), hydrogen peroxide (30 %, 1 mL), and potassium chloride (0.40 M, 0.1 mL) were combined in a 20 mL scintillation vial. The pH value was adjusted to 9 by adding of LiOH(aq) (4 M, 0.40 mL). After seven days, large, yellow, cubic crystals formed in solution. U36: Aqueous uranyl nitrate hexahydrate (2 M, 100 µL), hydrogen peroxide (30 %, 250 µL), and LiOH (4 M, 2 mL) were combined in a 20 mL scintillation vial. After six months, yellow equant crystals were recovered. U44: Aqueous uranyl nitrate hexahydrate (0.2 M, 2 mL) was combined with solid $KHSO_4$ (0.0695 g) in a 10 mL glass test tube. The resulting solution was stirred vigorously after the addition of aqueous solutions of NaOH (3 M, 0.5 mL) and hydrogen peroxide (30 %, 1.25 mL). After the resulting solution was held in ambient conditions for four days, a pH value of 6.67 was measured. Six days after the initial preparation, a portion of the solution (500 µL) was transferred to a 4 mL glass vial. A layer of [D]chloroform (99 %) was added, and the vial was capped. Yellow hexagonal, plate-like crystals 500 µm wide formed within three weeks. In all three cases, crystals were harvested upon formation, at which time the yields were on the order of 10 % or less.

X-ray diffraction: Diffraction data was collected for crystals of each compound at $T = 110$ K using a Bruker PLATFORM three-circle single crystal X-ray diffractometer equipped with a CCD detector and $Mo_{K\alpha}$ radiation. The data for each was corrected for adsorption semiempirically using the intensities of equivalent reflections. Structures were solved and refined using the SHELXTL (Bruker Advanced X-ray Solutions, Madison, WI, USA). Anisotropic displacement parameters were refined for uranium and potassium atoms, and isotropic displacement parameters were refined for all other atoms. U60: Space group $Fm\bar{3}$, $a = 37.884(2)$ Å, $R_1 = 7.87\,\%$ for 2162 $F_o \geq 4\sigma F_o$, $S = 1.13$, 211 refined parameters, $wR_2 = 26.5\,\%$. U36: Space group $P\bar{1}$, $a = 19.861(2)$, $b = 23.369(2)$, $c = 30.964(3)$ Å, $\alpha = 77.897(2)$, $\beta = 88.570(2)$, $\gamma = 89.136(2)°$, $R_1 = 6.36\,\%$ for 11501 $F_o \geq 4\sigma F_o$, $S = 0.82$, 1213 refined parameters, $wR_2 = 18.7\,\%$. U44: Space group $R\bar{3}$, $a = 20.924(1)$, $c = 77.814(3)$ Å, $R_1 = 5.90\,\%$ for 3681 $F_o \geq 4\sigma F_o$, $S = 0.97$, 298 refined parameters, $wR_2 = 19.2\,\%$. 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-420185 (U36), CSD-420184 (U44), and CSD-420183 (U60).

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