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Inorganic Fullerene Structures

Metal–Oxygen Isopolyhedra Assembled into Fullerene Topologies**

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Carbon-based fullerenes have received considerable attention since their discovery[1] and are currently being produced on an industrial scale.[2] Fullerenes are cage structures composed of 12 pentagons and several hexagons.[3] Many fullerene topologies are possible, but selection criteria favor a small subset.[4] C_{60} is the classic and most stable fullerene.[1] No smaller fullerene can be built without its topology containing adjacent pentagons, which destabilize the structure through increased curvature.[4] For fullerenes with less than 60 C atoms, it is thought that those with the fewest adjacent pentagons will be the most stable because they minimize strain.[4,5] Fullerenes with less than 60 C atoms exist, for example C_{50}, which can be stabilized as $C_{50}Cl_{10}$ by addition of Cl^- ligands.[6] This structure does follow the minimal pentagon adjacency rule, but theoretical calculations suggest that pure C_{50} will not because sphericity is substantially increased when the number of adjacent pentagons is increased to six, as compared to five in the case of $C_{50}Cl_{10}$.[7]

There is also considerable interest in inorganic fullerene-like materials; particular emphasis is on compounds such as MoS_2 that tend to form onion-skin-like structures with useful materials properties.[8–10] Molybdenum–oxygen heteropolyhedra have previously been found to form clusters with fullerene topologies, termed keplerates.[11,12] Our earlier discovery of spherical clusters of uranyl peroxide polyhedra containing 24, 28, or 32 hexagonal bipyramids suggests that large clusters of metal–oxygen isopolyhedra with fullerene topologies may be synthesized.[13] Of the three uranyl peroxide clusters described earlier, the 28-metal-ion cluster U28 has a fullerene topology with 12 pentagons and 4 hexagons, whereas the other two also contain squares in their topologies.

We propose that assembly of metal–oxygen isopolyhedra into nanoscale fullerene topologies may be facilitated by judicious selection of structural building units. The rules that govern the formation of metal–oxygen cages are of interest, as such materials could have a variety of applications, including catalysis and synthesis of advanced materials. Assembly of metal–oxygen isopolyhedra into conventional fullerene topologies can only occur if at least the following conditions are met:

1) Each polyhedron must link to exactly three other polyhedra, and the most stable structures will occur when the connections between the metal–oxygen polyhedra are by the sharing of polyhedral edges.
2) The polyhedra must be geometrically compatible with forming topological pentagons and hexagons.
3) The three linkages emanating from any given polyhedron should be approximately coplanar to facilitate the cage geometry.
4) Linkages between polyhedra should be consistent with the bond-valence requirements[14] of the shared polyhedral elements within the cage.

These conditions favor assembly of hexagonal bipyramids into fullerene topologies. This is especially true if the ligands at the apices of the bipyramids do not require significant additional bonding, which will favor coplanar linkages through the equatorial edges of the bipyramids. Hexagonal bipyramids are most common in the case of higher-valence actinides,[15] which contain actinyl ions in which O atoms correspond to the apices of the bipyramids. Consider a $(UO_2)^{2+}$ uranyl ion coordinated by six ligands arranged at the equatorial vertices of a hexagonal bipyramid. The bonds within the uranyl ion are strong, and bonding requirements of these O atoms are essentially met without additional bonding.[16] Uranyl bipyramids usually link into structural units only by the sharing of equatorial vertices, either with other uranyl bipyramids or other polyhedra containing higher valence cations. As a result, more than 60 % of the structures of inorganic uranyl compounds contain sheets of polyhedra with higher-valence cations.[17]

Considering sheets of uranyl polyhedra that occur in many minerals and synthetic compounds, pentagonal bipyramids dominate, with fewer hexagonal bipyramids. In most cases the bipyramids are connected to as many as six other uranyl polyhedra within the sheet.[17] The anions within the sheets are usually O^{2-} or OH^-, and are most often shared between three uranyl polyhedra. To facilitate cage formation, other ligands will be necessary. Peroxide provides an excellent route to transform the sheet-forming tendencies of uranyl polyhedra into cage-forming tendencies,[13] as insertion of peroxide along equatorial edges of an actinyl hexagonal bipyramid limits the number of connections it can make. The formal valence of peroxide is 2−, and each O atom of peroxide can form bonds to U^{6+}, totaling 1 valence unit. The typical valence of a U^{6+}–$O_{equatorial}$ bond in a hexagonal bipyramid is 0.44

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valence units.[17] At most it is possible for an O atom of a peroxide molecule to link to two uranyl ions, and such a linkage should be a stable configuration as the bond-valence requirements of the peroxide O atoms will be essentially satisfied. Insertion of two or three peroxide molecules along equatorial edges of a hexagonal bipyramid restricts the number of edges that the polyhedron can share with other uranyl polyhedra to three. Uranyl hexagonal bipyramids with two or three peroxide edges are therefore candidates for formation of fullerene topologies. The presence of peroxide edges should frustrate the tendency to form dense sheets of polyhedra, and to date the only actinyl peroxide sheet structure is highly porous.[18]

Several hundred strictly inorganic syntheses involving uranyl peroxide polyhedra in our laboratory failed to result in cage structures with more than 32 hexagonal bipyramids. Large clusters consisting of hexagonal bipyramids will encase considerable space, so it was hypothesized that organic molecules encapsulated in the cages might stabilize larger cages. However, peroxide can oxidize organic molecules and is fairly unstable. Earlier work has shown that peroxide complexed to uranyl ions is stable for geologic times in minerals.[19] Alkaline uranyl peroxide solutions were prepared and allowed to stand at room temperature for 7 days to permit the breakdown of peroxide in excess of that which coordinated uranyl. Many experiments were conducted with the addition of various organic molecules to the resulting solutions. In the case of a solvothermal reaction of the alkaline uranyl peroxide solution containing Li with amine molecules at 80 °C for 24 h, an unprecedented cage structure consisting of 50 uranyl hexagonal bipyramids was created when the heat-treated solution was allowed to stand at room temperature.

Single crystals containing the clusters were isolated, and their structure was determined by single-crystal X-ray diffraction. The cluster, hereafter designated U50, consists of uranyl hexagonal bipyramids linked into a fullerene topology with 12 pentagons as well as hexagons (Figure 1). Each hexagonal bipyramid contains two peroxide edges, and another edge is defined by two hydroxy groups. The cage has the composition $[\{(UO_2)(OH)(O_2)\}_{50}]$ and a net charge of -50, which is balanced by incorporation of Li ions and organic molecules into the structure. The maximum diameter of the cluster is 2.4 nm, as measured from the centers of bounding O atoms. The apical ligands of the hexagonal bipyramids that define the outer and inner surfaces of the cage correspond to O atoms of the uranyl ions, and as such are relatively unreactive.

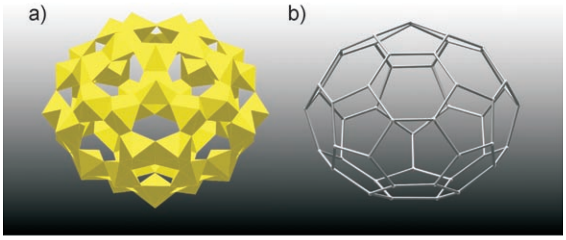

Figure 1. Structure of U50: a) polyhedral representation, with uranyl peroxide hexagonal bipyramids shown in yellow; b) connectivity diagram, in which nodes represent polyhedra and lines indicate shared edges between polyhedra.

The topological aspects of U50 are best illustrated by a connectivity diagram, in which vertices correspond to hexagonal bipyramids and lines designate shared edges between polyhedra (Figure 1 b). Of the 271 possible fullerene isomers with 50 vertices,[3] U50 adopts the isomer with minimal adjacent pentagons, identical to that of the $C_{50}Cl_{10}$ fullerene with D_{5h} symmetry, and not the most symmetrical isomer, which would require additional adjacent pentagons. U50 contains two isolated pentagons that are composed solely of shared peroxide edges, as well as five pairs of shared pentagons that contain four peroxide edges and one shared edge that consists of two hydroxy groups. The hexagons in U50 contain alternating peroxide and hydroxide edges, or two peroxide edges in a *trans* configuration within the hexagon.

By using different organic molecules under otherwise identical synthesis conditions, a cage cluster containing 40 uranyl hexagonal bipyramids was obtained (Figure 2). As in U50, the hexagonal bipyramids in U40 contain two peroxide edges as well as one edge defined by two hydroxy groups. The bipyramids in U40 are connected into 2 squares, 8 pentagons, and 12 hexagons, and the cluster has D_{2h} symmetry. There are four pairs of adjacent pentagons, which is fewer than in U50. The two squares in the topology are located about the major axis of the spheroid. The squares are adjacent to hexagons, and the shared edges of the hexagons alternate between peroxide and hydroxy edges of the bipyramids. Pentagons in U40 consist of four shared peroxide edges and one hydroxy edge. The peroxide edges are also part of the hexagons, whereas the hydroxy edge corresponds to an adjacent pentagon. The presence of squares in the U40 topology presumably alleviates strain associated with adjacent pentagons.

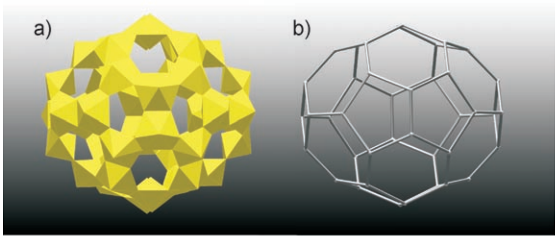

Figure 2. Structure of U40: a) polyhedral representation, with uranyl peroxide hexagonal bipyramids shown in yellow; b) connectivity diagram, in which nodes represent polyhedra and lines indicate shared edges between polyhedra.

The X-ray diffraction data did not reveal the position of the organic molecules within the cages of U40 and U50, although considerable electron density occurs within the cages that may be attributable to disordered organic molecules, as well as water, Li, and Na atoms. Infrared spectra confirmed that crystals of U40 and U50 contain organic molecules. The exact role of the amines in the formation of these clusters is currently unclear. Earlier syntheses of U24, U28, and U32[13] were achieved at room temperature, whereas treatment at 80 °C apparently facilitated the formation of crystals of U40 and U50. Peroxide stability in solution decreases with increasing temperature, and formation of crystals of U40 and U50 from heated solutions further illustrates that peroxide complexed to uranyl ions is much more stable than free peroxide.

In the case of U40, and the earlier reported clusters U24 and U32,[13] the presence of squares in the topology prevents direct comparison with the fullerene topologies. U28, in contrast, does form a fullerene topology that is based on uranyl triperoxide hexagonal bipyramids with overall T_d symmetry. Several C28 fullerene isomers have been predicted, including those with D_2 and C_s symmetry, but the most stable topology is likely to have T_d symmetry.[4] The existence of squares in some of the cage topologies containing hexagonal bipyramids dramatically increases the number of possible isomers relative to C-based fullerenes.

The presence of squares, pentagons, and hexagons in the topologies of structures containing uranyl hexagonal bipyramids is related to the positions of peroxide groups within the bipyramids. Figure 3 illustrates the arrangement of peroxide and hydroxy edges in cages of uranyl hexagonal bipyramids observed to date. Squares in U24, U32, and U40 always correspond to four shared peroxide edges, and there is little distortion of the square. Each of the structures of U28, U32, U40, and U50 contain pentagons. Usually the pentagons correspond to four peroxide edges and one edge consisting of two hydroxy groups, and this creates distortion of the angles within the pentagon. In U28 the pentagons correspond only to shared peroxide edges, and the same configuration occurs for the isolated pentagon in the topology of U50. All of the cages based on uranyl hexagonal bipyramids found to date contain hexagons, but there are three different configurations. Some correspond only to peroxide edges, some have edges that alternate between peroxide and edges defined by two hydroxy groups, whereas others have peroxide and hydroxy edges arranged in a *trans* configuration.

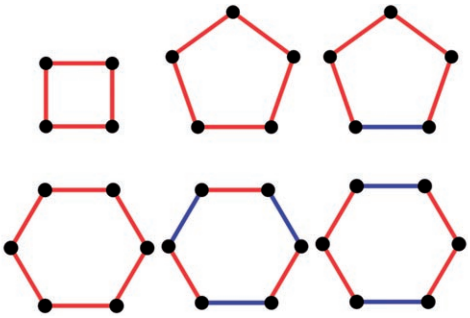

Figure 3. The arrangement of peroxide and hydroxy edges within the squares, pentagons, and hexagons that occur in U24, U28, U32, U40, and U50. Nodes represent uranyl peroxide hexagonal bipyramids. Lines represent shared edges between bipyramids. Shared peroxide edges are shown by red lines and blue lines correspond to shared hydroxy edges.

Relative to C-based fullerenes, cages built from hexagonal bipyramidal metal–oxygen isopolyhedra have many more possible isomers as a result of the possible inclusion of squares in their topologies. Despite this, U28 and U50 adopt conventional fullerene topologies with 12 pentagons and several hexagons. In the case of cages assembled from actinyl hexagonal bipyramids, it may be possible to tune the size, shape, and topology of the cages by changing the number and arrangement of peroxide edges in the bipyramids. The principles elaborated herein also provide insights into other types of metal–oxygen isopolyhedra that may be induced to form cages with fullerene topologies.

Experimental Section

A uranyl peroxide stock solution was created by adding LiOH solution (3 mL; 1 g LiOH in 10 mL H_2O) to 30 % H_2O_2 (1 mL). Uranyl nitrate solution (1 mL, 2 M) was slowly added to the LiOH/H_2O_2 solution, and the resulting solution was mixed thoroughly. After one week, stock solution (300 μL) was added to a 5-mL teflon vial with a snap-on lid. Ethylenediamine or tris(2-aminoethylamine) (30 μL) was added to the teflon vial for the syntheses of U40 and U50, respectively. The teflon vials were placed into a 125-mL teflon-lined Parr reaction vessel and heated at 80°C for 24 h. The solutions were transferred to glass vials and left untouched for two months. During that time, blocky yellow (ca. 200 μm) and large orange (ca. 2 mm) crystals formed containing U40 and U50, respectively, both in moderate yields.

X-ray diffraction data were collected at 110 K on a Bruker SMART APEX diffractometer ($\lambda = 0.71073$ Å). A sphere of data was collected for each crystal by using frame widths of 0.3° in ω. Data were corrected for Lorentz and polarization by using the Bruker program SAINT, absorption corrections were performed by using the Bruker program XPREP (version 5.1, 1997), and the structures were solved by direct methods and refined on the basis of F^2 for all unique reflections by using the Bruker SHELXTL suite of programs (version 5.10, 1997). Following refinement of the partial-structure models and calculation of difference-Fourier maps, it became apparent that the solvent and organic molecules contained within the structures are disordered. A correction for the electron density contained within the considerable void space was applied with the program SQUEEZE within the framework of PLATON.

Crystallographic data for U40: crystal dimensions 150 × 110 × 100 μm^3, monoclinic, $C2m$, $a = 36.876(3)$, $b = 24.668(2)$, $c = 25.815(2)$ Å, $\beta = 132.930(1)°$, $V = 17{,}194.1(1)$ Å^3, $\mu = 18.3$ mm^{-1}, $R_1 = 3.02\,\%$, $wR_2 = 6.37\,\%$, 178774 total reflections, 36812 unique reflections, 19833 unique reflections with $F_o \geq 4\sigma$. Crystallographic data for U50: crystal dimensions 200 × 150 × 100 μm^3, monoclinic $P2_1/n$, $a = 26.77(3)$, $b = 38.80(3)$, $c = 47.33(5)$ Å, $\beta = 103.24(4)°$, $V = 47{,}851.86$ Å^3, $\mu = 16.9$ mm^{-1}, $R_1 = 8.02\,\%$, $wR_2 = 19.24\,\%$, 418,106 total reflections, 62,552 unique reflections, 21043 unique reflections with $F_o \geq 4\sigma$. 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-419052 and CSD-419051.

Infrared spectra were obtained for single crystals on a SensIR technology IlluminatIR FT-IR Microspectrometer. A single crystal of each compound was placed on a glass slide, and the spectrum was collected with a diamond ATR objective. The spectra were taken from 400 to 3600 cm^{-1} with an aperture of 100 μm.

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