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Properties and applications of nanoscale actinide cage clusters

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Uranyl peroxide cage clusters self-assemble from aqueous solution under ambient conditions. To date, we have isolated more than 80 distinct clusters that differ in the number of uranyl ions, size, and topology. These clusters contain from 18 to 124 uranyl ions, and are from 1.5 to 4 nm in diameter. Most are readily soluble in aqueous solution. Although peroxide bridges between uranyl ions are thought to be essential for cage cluster formation, other bridges are also incorporated into the clusters, including phosphate, oxalate, pyrophosphate, nitrate, hydroxyl, tungstate, and phosphite.

The topologies of uranyl peroxide cage clusters vary dramatically. Several have fullerene topologies consisting of 12 pentagons as well as hexagons, whereas others consist of combinations of topological squares and hexagons. Several, including U60, are topologically analogous to C fullerenes. The largest cluster, containing 124 uranyl ions, consists of four cages in a tetrahedral arrangement, and an additional cage at the center of the tetrahedron. The properties of the cage clusters, including stability and aqueous solubility, appear to be related to the details of the topologies.

Uranyl peroxide cage clusters are crystallized for structural characterization, and characterized in solution using a combination of small-angle X-ray scattering (SAXS), electrospray ionization mass spectrometry (ESI-MS), dynamic light scattering (DLS), static light scattering (SLS), transmission electron microscopy (TEM), and nuclear magnetic resonance spectroscopy (NMR). At low concentrations these clusters persist as monomers in solution for months or longer, and undergo dynamic interchange between conformations in some cases. At higher concentrations, aggregation occurs to form "blackberries" that have well defined shapes and sizes.

One potential application of uranyl peroxide cage clusters is for recovery of uranium from nuclear materials, such as irradiated nuclear fuels. Specifically, uranium oxide fuel can be dissolved under alkaline aqueous conditions in the presence of peroxide, which both oxidizes the U(IV) to U(VI) and bridges the uranyl ions, forming cage clusters. These clusters may then be recovered from solution by filtration through a porous membrane. Complicating factors include blackberry formation and association of counterions with the anionic cage clusters.

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