Rapid Self-Assembly of Uranyl Polyhedra into Crown Clusters

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S *Supporting Information*

ABSTRACT: Clusters built from 32 uranyl peroxide polyhedra self-assemble and crystallize within 15 min after combining uranyl nitrate, ammonium hydroxide, and hydrogen peroxide in aqueous solution under ambient conditions. These novel crown-shaped clusters are remarkable in that they form so quickly, have extraordinarily low aqueous solubility, form with at least two distinct peroxide to hydroxyl ratios, and form in very high yield. The clusters, which have outer diameters of 23 Å, topologically consist of eight pentagons and four hexagons. Their rapid formation and low solubility in aqueous systems may be useful properties at various stages in an advanced nuclear energy system.
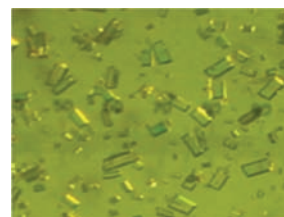
Figure 1. Crystals containing U_{32R} clusters that formed within minutes in aqueous solution. The horizontal field of view is about 1000 μm.

Polyoxometalates based upon transition metals have been extensively studied,[1] but until recently only a few contained actinides.[2] Duval[3] reported a polyoxometalate cluster containing U^{5+}, and we have reported 27 different nanoscale clusters built from as many as 60 U^{6+} uranyl hexagonal bipyramids,[4−9] as well as oxalate or pyrophosphate in some cases. All of these contain peroxide groups that bridge between uranyl ions, and computational studies have shown that covalent interactions between the peroxide and uranyl ions cause the $U−(O_2)−U$ unit to be bent.[10] It is this bent configuration that favors formation of cage clusters, rather than the sheets of uranyl polyhedra that are typical of minerals and synthetic compounds.[6]

Clusters of actinide elements, especially those that self-assemble rapidly under ambient conditions, have potential major applications in an advanced nuclear energy system. For example, such clusters may be used to separate actinides from complex solutions on the basis of size or mass and would provide nanoscale control of composition as precursors in the manufacture of novel nuclear fuels and waste forms.

Cluster U_{32R} spontaneously self-assembles in aqueous solutions following the combination of uranyl nitrate, hydrogen peroxide, and ammonium hydroxide in water. It assembles and crystallizes within 15 min. These crystals reach diameters of hundreds of micrometers within minutes (Figure 1), and representative crystals were isolated for diffraction studies shortly after they formed.

Crystal structure analyses of crystals that grew in three different experiments revealed topologically identical clusters, each consisting of 32 uranyl ions present as UO_8 in hexagonal bipyramids (Figure 2). These bipyramids share two or three equatorial edges with adjacent bipyramids, resulting in novel crown-shaped clusters. The uranyl ions have typical geometries, with $U−O$ bond lengths of ∼1.8 Å and $U−O−U$ bond angles of ∼180°. Three chemically distinct clusters were crystallized, as

distinguished by the coordination environments of the uranyl ions. The first of these, U_{32R-1}, contains eight uranyl ions that are coordinated by three peroxide groups located along equatorial edges of hexagonal bipyramids (designated triperoxide bipyramids). It also contains 24 uranyl ions that are coordinated by two peroxide groups and two OH groups, arranged such that two of the equatorial edges of the bipyramids are peroxide groups, and another edge is defined by the two OH groups (designated diperoxide bipyramids). The crystallographic analysis indicates this cluster has composition $[(UO_2)_{32}(O_2)_{40}(OH)_{24}]^{−40}$; NH_4^+ cations provide charge balance. The second of these, U_{32R-2}, contains 16 diperoxide and 16 triperoxide bipyramids. The cluster composition is $[(UO_2)_{32}(O_2)_{44}(OH)_{16}]^{−40}$. The third, U_{32R-3}, contains both diperoxide and triperoxide bipyramids, but some of the O−O bond separations along equatorial edges of the bipyramids derived from the crystallographic study are ∼2.0 Å, which is intermediate between a peroxide O−O bond length (∼1.5 Å) and the O···O separation of a OH··· OH edge (∼2.6 Å). Crystals of U_{32R-3} present an average cluster geometry consistent with coprecipitation of clusters having the compositions of the U_{32R-1} and U_{32R-2} clusters.

The U_{32R} cluster is 23.0 Å by 17.3 Å, as measured from the outer edges of the bounding O atoms. It has an inner free space that is 7.9 Å, but the lips at the top and bottom of the cluster protrude inward, and the resulting openings at the top and bottom have free diameters of 5.2 Å.

A topological representation of the U_{32R} clusters is shown in Figure 2c. Each vertex represents a U cation, and lines designate bridges between the corresponding uranyl ions, through either OH···OH or peroxide edges. It contains eight pentagons and four hexagons. The pentagons are grouped such that pairs share an edge, and these dimers of pentagons are connected through the hexagons, giving the crown topology.

In cluster U_{32R-1}, triperoxide bipyramids only occur at the top and bottom, where they share two peroxide edges with adjacent diperoxide bipyramids (Figure 2a). The third edge that
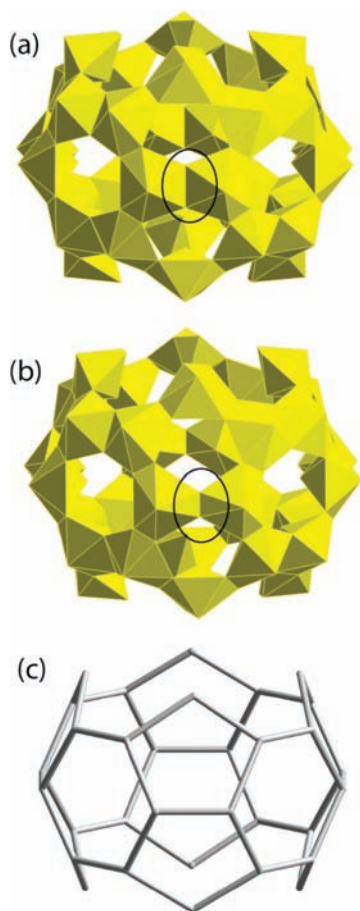
Figure 2. U_{32R} clusters of uranyl peroxide polyhedra. (a) Polyhedral representation of U_{32R-1}. (b) Polyhedral representation of U_{32R-2}. (c) Topological graph with vertices corresponding to U cations and connectors representing bridges between uranyl ions.

corresponds to peroxide is not shared in the cluster. All of the diperoxide bipyramids share three edges with other biyramids within the cluster. In U_{32R-2}, there are eight triperoxide bipyramids at the edges of the cluster, analogous to U_{32R-1}, and eight triperoxide bipyramids are located around the equatorial of the cluster. In Figure 2 an ellipse indicates the shared edge that corresponds to OH···OH in U_{32R-1} and peroxide in U_{32R-2}.

There are at least four noteworthy aspects of the synthesis and isolation of the U_{32R} clusters. The first is that these are a new cluster type with a unique crown topology. They are larger than the crown topologies we reported earlier, which contained 20 and 24 uranyl ions.[8] The topology of U_{32R-1} is closely related to the U_{36} cage cluster[7] and can be topologically derived from it by simply deleting two uranyl ions from both the top and the bottom of the cluster.

The second notable feature is the rapid self-assembly and crystallization of the U_{32R} clusters. This occurs within 15 min of mixing the reactants and gives well-formed crystals measuring ~100 μm suitable for X-ray diffraction. The uranyl ions are added to the aqueous solution as uranyl nitrate, with peroxide added separately. In minutes or less peroxide replaces nitrate at the equatorial edges of uranyl hexagonal bipyramids, and the bipyramids self-assemble into the U_{32R} clusters. We emphasize that this is a simple, one-pot reaction conducted under ambient conditions. The aqueous solubility of these clusters must be low,

as they precipitate extremely fast under a yellow solution. Given that only crystals of U_{32R} are obtained, as verified by single-crystal X-ray diffraction on dozens of crystals, the yield (relative to U) is high. In contrast, many of the clusters of uranyl ions we have reported earlier take weeks or more to crystallize,[5] some do so only when the mother solution is allowed to evaporate, and small-angle X-ray scattering (SAXS) studies have shown that significant concentrations of such clusters remain in solution.[5,9] In addition, the SAXS data typically indicate polydispersion of the clusters in solution. For polyoxometalates in general, reported synthesis methods often require extended periods of heating, solution aging, or solution evaporation.

Remarkably, the chemical composition of the U_{32R} clusters is almost indistinguishable from several other clusters we have synthesized, and these remain in solution for months. Although it is unique, the U_{32R} topology is built from hexagons and pentagons, as are several others we have studied. Even the topologically closely related U_{36} cage cluster only crystallized after several days. The low aqueous solubility of the cluster most likely is related to the crown-shaped topology, specifically to the eight peroxide groups that truncate the ends of the cluster. However, similar nonbridging peroxide groups occur in other crown clusters we reported earlier, and these did not crystallize rapidly.[8]

The third notable feature is that crystals of U_{32R} in contact with their mother solution under ambient conditions disappear after 6 h. The assembly of U_{32R} clusters is apparently kinetically favored. As the U_{32R} clusters that remain in solution are replaced by other clusters or uranium species, the crystals dissolve, and a fine-grained amorphous precipitate forms.

The fourth notable feature of the U_{32R} clusters is that they can be crystallized with different quantities of peroxide and hydroxyl. Experiments with the highest uranium to peroxide ratios in solution give clusters with the most peroxide. Yet, despite their different compositions, clusters of U_{32R} all self-assemble at an extraordinary rate and crystallize quickly.

The rapid self-assembly and precipitation of U_{32R} or similar clusters in aqueous solution may be useful for the separation of U from various elements in solution, as is necessary at various stages in the nuclear fuel cycle.

■ ASSOCIATED CONTENT

S **Supporting Information.** Experimental methods, crystallographic data for all compounds, X-ray powder diffraction data for the fine-grained precipitate, crystallographic information files for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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