Hybrid Uranyl Arsonate Coordination Nanocages

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S *Supporting Information*

ABSTRACT: Nanoscopic uranyl coordination cages have been prepared by a facile route involving self-assembly via temperature and solvent-driven, in situ ligand synthesis. The synthesis of hydrogen arsenate and pyroarsonate ligands in situ enhances flexibility, which is an important factor in producing these compounds.

The synthesis of uranyl nanotubes[1] and nanospheres[2] has been the focus of numerous recent studies inspired by the prospect of tailoring the properties of nanoscale materials for use in an advanced nuclear energy system.[2b,c] Although a family of more than 40 uranyl peroxide cage clusters has been developed, it is extremely rare for uranyl–organic discrete compounds to form nanoscale cages or clusters.[3a] In contrast to progress in nanospheric transition-metal materials with emerging applications,[3b,c] the design of nanoscale uranyl materials from hybrid inorganic–organic discrete compounds remains an elusive goal. The lack of coordination along the axial position of the uranyl ion favors the formation of chains or sheets of uranyl polyhedra. The formation of well-organized nanospherical uranyl structures in the absence of peroxide is a considerable challenge, expecially when planar aromatic ligands are employed.[4] One approach to overcoming this is to use pliable phosphonate derivatives to introduce curvature in structural units containing uranyl polyhedra, as we have demonstrated for functional uranyl diphosphonate nanotubes and a bimetallic uranyl heteropolyoxometalate.[1f,g,5]

Inspired by our previous accomplishments with uranyl phosphonates, our laboratory began to investigate the structural chemistry and physicochemical properties of uranium arsonates. Reports of uranyl arsonates have only appeared recently.[6] Although arsenic(V) and phosphorus(V) are neighboring pnictogens, a relatively small difference in the ionic radii and bond lengths can produce dramatic structural differences, as exemplified in our recent report in which phenylarsonate ligands were fused to form the pyroarsonate moiety in $UO_2(C_6H_5)_2$-$As_2O_5(H_2O)$.[6] In marked contrast to other reported metal pyroarsonates that were obtained under solvothermal conditions (mostly prepared with acetonitrile as the solvent), $UO_2(C_6H_5)_2As_2O_5(H_2O)$ was prepared under hydrothermal conditions. The synthesis of the pyroarsonate ligand in situ enhances flexibility, which is an important factor for producing novel structural topologies. In an expansion of our work with arsonates, we are probing how a variety of solvents affect the reactions between uranyl cations and phenylarsonate at different temperatures.

Herein we demonstrate that two exceptional nanoscale uranyl arsonate discrete compounds with spherical morphologies are assembled with UO_2^{2+}, using flexible phenylarsonate derivatives via in situ ligand synthesis (see Figure 1).[7] The overall
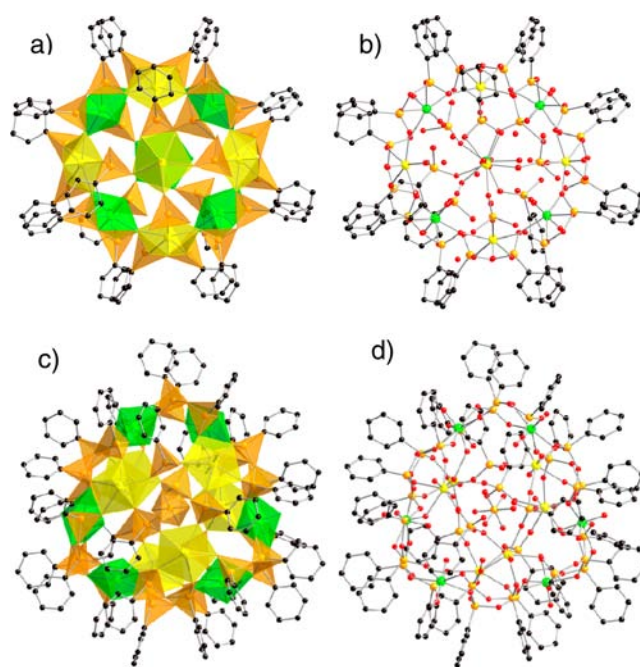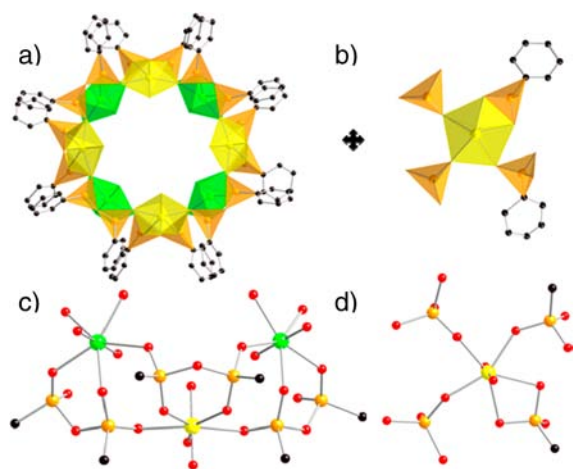

Figure 1. Both polyhedral and ball-and-stick representations of **1** (a and b) and **2** (c and d). Color code: uranium, yellow/green; arsonate, orange; oxygen, red; carbon, black. Hydrogen atoms are omitted for clarity.

structure of $[H_3O]_6\{(UO_2)_{10}[(C_6H_5)_2As_2O_5]_8(C_6H_5AsO_3)_2(C_6H_5AsO_3H)_2(H_2AsO_4)_4(H_2O)_3\}\cdot 2H_2O$ (**1**), is composed of cyclic uranyl pyroarsonate units that are capped on both sides by uranyl cations, forming nanoscopic cages approximately 14.2 × 13.6 Å in diameter, as measured from the centers of the outer oxygen atoms of the uranyl cations. The anionic cage consists of 10 monomeric uranyl cations in two subgroups on the basis of their coordination environments: eight uranyl cations are bound by eight pyroarsonate moieties (Figure 2a), and the remaining two uranyl cations are each coordinated by two hydrogen arsenates and two phenylarsonates (Figure 2b). This structure is distinct from hybrid uranyl–organic cage clusters recently published by Burns and co-workers in which the organic moieties
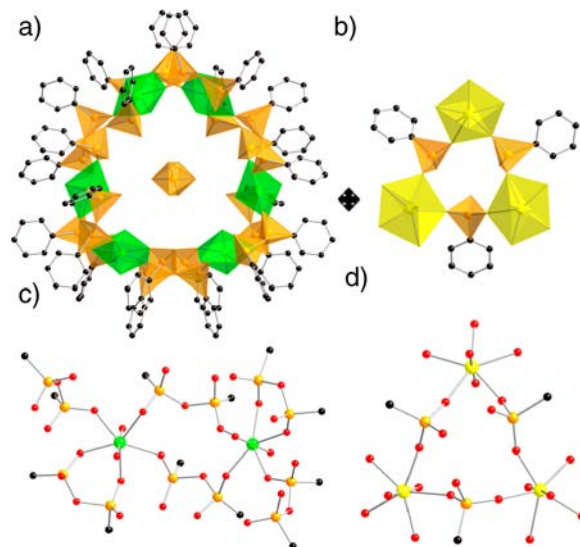
Figure 2. Polyhedral representations of the cyclic uranyl pyroarsonate moiety (a) and the capping uranyl arsonate arsenate unit (b) in **1**. Ball-and-stick representation of the two coordination environments observed around the uranyl cations in **1** (c and d). The phenyl groups have been truncated for clarity. Legend as in Figure 1.

(i.e., oxalate and methylenediphosphonate) bridged between the uranyl ions in peroxide polyoxometalate clusters.[8] Another fascinating feature that distinguishes the structure of **1** from other uranyl coordination nanocages[3a] is the assembly of the central inorganic core from uranyl cations and oxoanions (hydrogen arsenates, arsonates, and pyroarsonates). The phenyl rings are arranged on the outer periphery of the spherical core. However, the calixarene carboxylate ligands form part of the nanospheric core in the calixarene−uranyl capsules.[3a]

The monomeric uranyl ions are part of the pentagonal-bipyramidal coordination polyhedral UO_7. The O=U=O uranyl ion bond angles range from 175.8(5)° to 179.6(5)°, with typical U=O_{axial} bond distances ranging from 1.740(16) to 1.818(11) Å. Five oxygen atoms are coordinated to the uranyl center in the equatorial plane with U−O bond distances that range from 2.200(17) to 2.532(17) Å. The calculated bond-valence sums for the uranyl cations are consistent with the formal valence of uranium(VI).[9] Their oxidation state is further substantiated by the absorption spectrum (see the Supporting Information). The most remarkable portion of the synthesis is the metal-mediated, thermally induced condensation process in which the phenylarsonic acid units are combined in situ to form the fused tetrahedra of the pyroarsonate moiety, $[PhAs(O_2)-OAs(O_2)Ph]^{2-}$.

The pyroarsonate ligands are pliable, providing the necessary curvature for the formation of **1**.[10] The As−O bond distances from the pyroarsonate ligands range from 1.636(11) to 1.792(10) Å. The As−O−As linkages are noticeably longer than the rest of the As−O bonds. These distances are within the ranges expected for pyroarsonate.[6] The As−O bond distances from the phenylarsonate ligands range from 1.600(19) to 1.996(13) Å. The longest As−O bonds correspond to the terminal oxygen groups and reveal the presence of protonated arsonate groups. Although the hydrogen arsenate group is disordered in the crystal structure, it plays a similar role as phenylarsonate and is generated in situ via decomposition of some of the ligands. It is unlikely that these arsenate anions exist as AsO_4^{3-} because four of $H_2AsO_4^-$ are essential for charge-balancing to give an overall neutral species, and $H_2AsO_4^-$ is more likely to be found under the synthetic condition of pH ~ 2.

The structure of $[H_3O]_6\{(UO_2)_{12}[(C_6H_5)_2As_2O_5]_{12}$-$(C_6H_5AsO_3H)_6(H_2O)_5[H_2AsO_4(H_2O)_2][H_3O]\}\cdot H_2O$ (**2**) resembles **1** in that they are both constructed from uranyl monomers and the uranyl ions are coordinated by pyroarsonate and phenylarsonate groups to form nanoscale coordination cages. This cage is approximately 16.4 × 16.2 Å in diameter, measured from the centers of the outer oxygen atoms of the uranyl cations. Two unique coordination environments are formed around the uranyl cations: six uranyl cations (green in Figure 3) that are bound by 12 pyroarsonate moieties (Figure 3a)
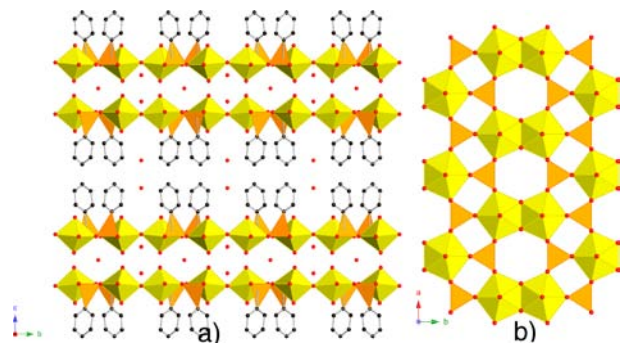

Figure 3. Polyhedral views of the uranyl pyroarsonate moiety (a) and the capping triangular uranyl phenylarsonate moiety (b) in **2**. Ball-and-stick representations of the two coordination environments observed around the uranyl cations in **2** (c and d). The phenyl groups have been truncated for clarity. Legend as in Figure 1.

and three uranyl cations that form a triangular unit, as shown in Figure 3b. These three uranyl cations are connected by three phenylarsonates and form the top and base of the uranyl coordination cage. One of the most striking features of this structure is the encapsulation of a rare six-coordinate hydrogen arsenate species in octahedral coordination, which is located in the center of the cage, as shown in Figure 3a.

The structure of **2** is composed of monomeric uranyl cations present as UO_7 pentagonal bipyramids that are linked through the arsonate oxygen atoms. All of the uranium cations are coordinated by two nearly linear oxo atoms, forming a UO_2^{2+} unit, and the O=U=O bond angles range from 176.2(14) to 178.9(10)°, with U=O bond distances ranging from 1.689(13) to 1.808(19) Å. The coordinated five oxygen atoms in the equatorial plane are at typical values for the U−O bond distances. The calculated bond-valence sums at the uranium centers and the absorption spectrum are in agreement with uranium(VI) (see the Supporting Information).[9] The As−O bond distances from phenylarsonates range from 1.625(13) to 1.690(13) Å, and pyroarsonate moieties are between 1.606(12) and 1.999(13) Å (certain bond lengths are outside the normal range as a result of disordered atoms). The composition of the hydrogen arsenate group is formulated as $[(H_2AsO_4)(H_2O)_2][H_3O]$ because the $H_2AsO_4^-$ species is the expected moiety at the reaction conditions. This formulation is speculative and based solely on the crystal structure wherein the arsenate group is

six-coordinate. The hydronium ion is assumed in both **1** and **2** to balance the overall charge.

To evaluate the factors necessary for the formation of pyroarsonate in situ, reactions were performed under various solvent conditions at different temperatures. However, a similar reaction that produced **1** and **2** in a MeCN/2-propanol mixture yielded a layered uranyl arsonate coordination polymer $(UO_2)_2\text{-}(O_3AsC_6H_4)_2\cdot 3H_2O$ (**3**) at 140 °C. Similar solvothermal reactions in methanol, ethanol, and 2-propanol at 160 °C also afforded **3** (see Figure 4). We infer from these results that the

Figure 4. Polyhedral view of the layered uranyl arsonate coordination polymer (a) and illustration of the uranyl sheets (b) in **3**. Legend as in Figure 1.

formation mechanism of the pyroarsonate moiety is both solvent- and temperature-dependent. This is somewhat speculative based solely on the isolated product, and further work is necessary to substantiate this claim and demonstrate how the pyroarsonate ligands are generated in both aqueous and organic solvents at different temperatures.

Uranyl-containing compounds often exhibit luminescent properties. The fluorescent spectra for **1**−**3** show strong vibronic coupling near 520 nm, yielding a well-resolved five-peak pattern. The IR spectra confirm the characteristic peaks for stretching modes of the uranyl cation, around 819 cm^{-1} in **1**, 838 cm^{-1} in **2**, and 867−908 in **3**. Those bands at 1101, 1095, and 1093 cm^{-1} are assigned to $\nu(As=O)$ stretches of **1**−**3**, respectively. The C−H bending of the phenyl ring is positioned at 1444 cm^{-1} for **1**, 1441 cm^{-1} for **2**, and 1440 cm^{-1} for **3**. The broad band around 1600 cm^{-1} is indicative of H_2O bending, and the high-energy regions are dominated by the OH stretches of the lattice water (see the Supporting Information).

In summary, the assembly of highly unusual hybrid uranyl arsonate coordination nanocages described herein demonstrates that monomeric uranyl cations can be connected via flexible arsonate derivatives into uranyl nanospheres. Capitalizing on the in situ synthesis of ligands, the condensation reactions of organic ligands, if well-harnessed, can lead to the development of a series of uranyl compounds with novel structural topologies that are inaccessible without in situ ligand synthesis. These results provide supportive evidence that the metal cations, solvents, and temperature play vital roles in the condensation reactions. Compounds **1** and **2** are rare examples of hybrid uranyl organic coordination nanocages.[3a]

■ ASSOCIATED CONTENT

ⓈSupporting Information

X-ray crystallographic files in CIF format for compounds **1**−**3**, packing diagrams, photographs of yellow-green tablets, absorption, fluorescence, IR spectra, details of synthesis and structure determination, and SEM−EDX analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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