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Hybrid Uranyl-Vanadium Nano-Wheels

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Hybrid uranyl-vanadium oxide clusters intermediate between transition metal polyoxometalates and uranyl peroxide cage clusters were obtained by dissolving uranyl nitrate in the ionic liquid 3-Ethyl-1-methylimidazolium ethylsulfate mixed with an aqueous solution containing vanadium. Where sulfate was present, wheel-shaped $\{U_{20}V_{20}\}$ crystallized and contains ten sulfate tetrahedra, and in the absence of added sulfate, $\{U_2V_{16}\}$, a derivative of $\{V_{18}\}$, was obtained.

Metal oxide clusters with sizes ranging over a few nanometers exhibit beautiful architectures with useful properties, in part owing to their well-defined structures and size-dependent behavior.[1] Despite societal importance stemming from use as fuels for nuclear reactors and weapons, as well as environmental hazards due to wastes from these activities, development of the cluster chemistry of actinides has been slow because of their radioactivity, toxicity, and limited availability. Whereas transition metal (mostly Mo and W) oxide clusters (polyoxometalates) have been intensely studied for decades,[2] the first major family of uranium clusters has only emerged over the past decade.[1e, 1f, 3] The latter form with topological complexity and sizes that rival those of transition metals.

U(VI) uranyl ions invariably contain two "yl" O atoms in a *trans* arrangement. Transition metal oxide polyhedra in clusters often contain a single "yl" O atom, or two in a *cis* arrangement.[1e] The "yl" O atoms of clusters stabilize their surfaces, and in uranyl clusters nanocapsules dominate because "yl" O atoms often define both inner and outer surfaces. The different coordination environments of transition metals and uranium generally produce distinct clusters, and peroxide bridges between uranyl ions are thought to favor curved walls.[4]

We are interested in hybrid transition-metal uranyl clusters assembled without including peroxide ligands because they are expected to present interesting structures and properties intermediate between transition metal and uranyl clusters. Here we report a route to uranyl-vanadyl clusters by utilizing ionic liquid as a reaction medium. Intense interest in ionic liquids, including in actinide chemistry, arises from their novel combination of low melting point, low vapor pressure, high density, and high viscosity.[5] In addition to being the solvent, ionic liquids are a source of counter ions, ligands, and space-directing agents. They have been used in the synthesis of a few transition-metal polyoxometalates, and are under study for applications in processing of spent nuclear fuel.[5a] We report the synthesis and structures of novel uranyl-vanadium clusters $(EMIm)_{15}Na_5[(UO_2)_{20}(V_2O_7)_{10}(SO_4)_{10}]\cdot 80H_2O$ (**1a,b**) and $(EMIm)_8[(UO_2)_2(V_{16}O_{46})]\cdot xH_2O$ (**2**).

Crystals of **1a** were first obtained by liquid-liquid diffusion of an aqueous solution of sodium metavanadate into the ionic liquid 3-Ethyl-1-methylimidazolium ethyl sulfate (*EMIm-SO4Et*) containing dissolved uranyl nitrate, with a system molar ratio of 3:1 for V:U. The slow hydrolysis of ethyl sulfate provided sulfate for incorporation in **1a**, which crystallized after several months. Addition of a small amount of H_2SO_4 or $VOSO_4$ increased the reaction rate, giving crystals in as little as one week. In the absence of added H_2SO_4 or $VOSO_4$, crystals of **2** were recovered after one week in low yield (see Supporting Information). Our efforts to increase yield and purity demonstrated that layering of the aqueous and ionic liquids is unnecessary. Pure products were obtained by mixing the components, followed by removing a precipitate that formed immediately by filtration. Compound **1a** is the preferred product and crystalized over a broad range of $UO_2(NO_3)_2/NaVO_3$ ratios, and the presence of H_2SO_4 or $VOSO_4$ as additional sulfate sources increases the reaction rate. Crystals of **1b**, which contains the same uranyl vanadate cluster but in a different packing arrangement, formed in some experiments (see Supporting Information).
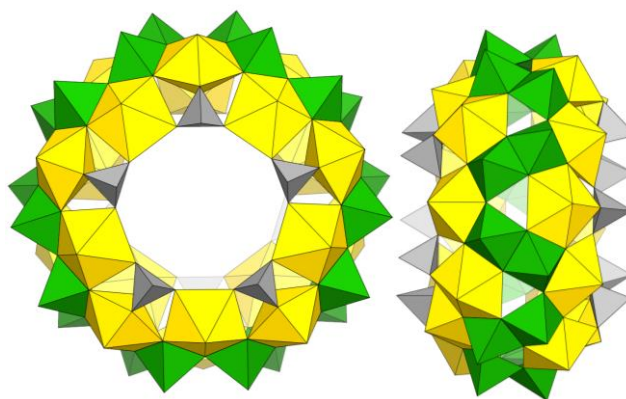
Figure 1. $\{U_{20}V_{20}\}$ wheel cluster **1a/b** constructed from uranyl pentagonal bipyramids (yellow), vanadate square pyramids (green), and sulfate tetrahedral (grey).

Analysis of the structure of **1a** using X-ray diffraction data revealed that it contains a novel wheel-shaped cluster, $\{U_{20}V_{20}\}$, with point group symmetry D_{5d} and a maximum diameter of 21.9 Å, measured from the outer edges of bounding O atoms. The cluster is built from 20 uranyl pentagonal bipyramids, 20 vanadate square pyramids, and 10 sulfate tetrahedra. The U≡O bonds of the nearly linear $(UO_2)^{2+}$ uranyl ions are typical,[6] with an average length of 1.775 Å, and the average U-O equatorial bond length is 2.374 Å. The

apical, non-bridging oxygens of the vandate square pyramids have an average V=O bond length of 1.595 Å, and the average V-O bond length for the base of the pyramids is 1.871 Å. Bond-valence calculations confirm the pentavalent and hexavalent oxidation states of vanadium and uranium, respectively (Supporting Information).

The arrangement of polyhedra in $\{U_{20}V_{20}\}$ is unique. There are two ten-membered rings of uranyl pentagonal bipyramids in which each bipyramid shares an equatorial vertex with a bipyramid on either side, with rigidity provided by five tridentate sulfate tetrahedra that are arranged on one side of the ring of bipyramids. Symmetrically identical uranyl sulfate units, in opposite orientations and rotated by 36°, are linked through dimers of vanadate square pyramids within which the vanadate polyhedra share an equatorial edge. Ten such V_2O_8 units are linked into a ring by sharing vertices in the equatorial region of the $\{U_{20}V_{20}\}$ wheel. The sharing of equatorial edges and vertices between the uranyl and vanadate polyhedra results in the overall cluster (Figure 1).

The vanadyl V=O bonds are directed away from the cluster, where, together with uranyl O atoms, they truncate it. On the inside of the wheel, O atoms of uranyl ions and the square faces of vanadate square pyramids terminate the uranyl vanadate sulfate cluster. The dimers of vanadate square pyramids are distinct from the many carnotite-type uranyl-vanadium compounds containing alkali and organic cations in which the two vanadyl V=O bonds of each dimer point in opposite directions, consistent with their sheet structural units.[7] In $\{U_{20}V_{20}\}$ electrostatic repulsion is responsible for the 44.1° tilt angle between the V=O units. In cases where $\{V_2O_8\}$ dimers containing vanadyl units that point in the same direction occur in sheet structural units, they impart a significant corrugation to the layer.[8] Vanadium square pyramids also organize into nanoscale molecular oxide bowls like $\{V_{12}O_{32}\}$ [9] and various spherical structures.[10]

The $\{U_{20}V_{20}\}$ wheel contains two ten-sided windows with free diameters of 6 Å. The cluster encapsulates 10 cation sites that are partially occupied by Na and 10 H_2O groups, which together are arranged as a pentagonal gyrobicupola (Figure 2, according to Johnson's nomenclature[11]). Each Na cation is bonded to four O atoms of uranyl ions, with bond lengths in the range of 2.28 to 2.64 Å. Two H2O groups complete the coordination environment of each Na, and the 10 H_2O are in a pentagonal arrangement on the top and bottom of the pentagonal gyrobicupola (Figure 2 and Supporting Information). Clusters are stacked directly over each other along [001], and the shortest distance between the terminal O atoms of sulfate tetrahedra of adjacent clusters is 3.70 Å (Figure 3). The spaces between the clusters contain EMIm cations, only some of which are localized, as well as disordered H_2O.

In a system that differed from that of **1** by having higher vanadium concentrations and no $VOSO_4$ or H_2SO_4, $\{U_2V_{16}\}$ (**2**) clusters crystallized. Unlike **1**, X-ray diffraction data indicate that **2** contains no sulfate, presumably due to restricted hydrolysis of SO_4Et under these conditions. The major structural component of $\{U_2V_{16}\}$ is distorted vanadate square pyramids, $\{VO_5\}$, 14 of which share edges to form a rigid ring that is two polyhedra wide. Two uranyl pentagonal bipyramids and two vanadium square pyramids complete the cluster (Figure 4) by sharing polyhedral vertices with the ring of polyhedra. The resulting cluster is similar to the polyvanadate anion $\{V_{18}\}$ reported earlier,[12] but with one $(UO_2)^{2+}$ incorporated on each of the top and bottom. In the crystal structure the anionic $\{U_2V_{16}\}$ units are surrounded by *EMIm* cations (see Supporting Information).
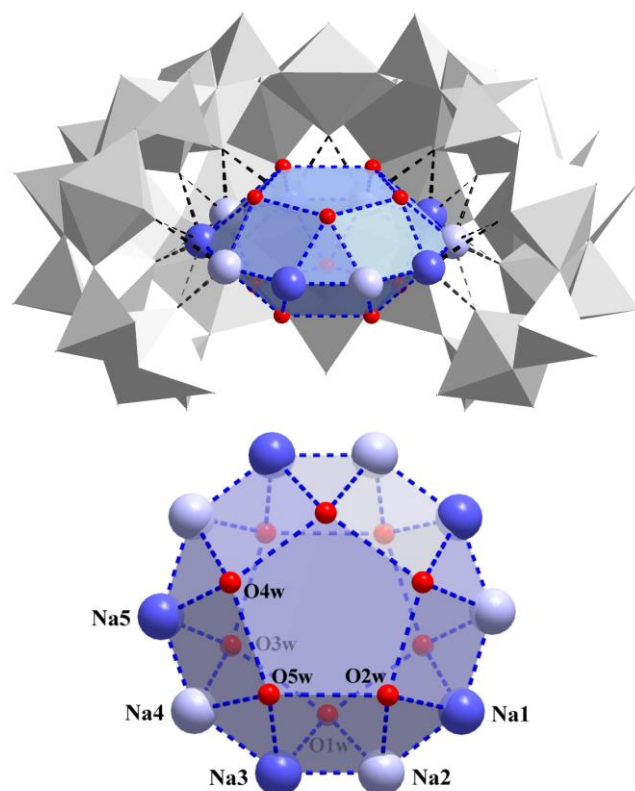
Figure 2. The Na cations (purple and light purple) and H_2O groups (red) located inside $\{U_{20}V_{20}\}$ define a pentagonal gyrobicupola. The $\{U_{20}V_{20}\}$ wheel cluster is shown as grey polyhedra, with the front portion omitted.
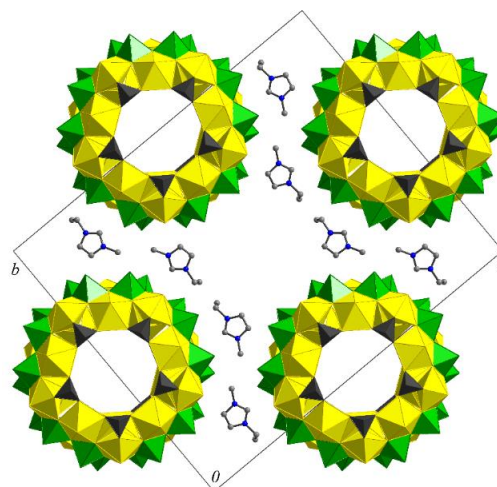
Figure 3. Packing of $\{U_{20}V_{20}\}$ wheels in the *ab* plane projected along the *c* axis in **1a**. EMIm cations are located between the clusters.

Transition metal oxide clusters with uranium polyhedra (or another actinide) as connectors between heteropolyoxometalate anions have been reported.[13] The $\{U_2V_{16}\}$ cluster is a derivative of $\{V_{18}\}$,[12] but there is no analogue of $\{U_{20}V_{20}\}$. Of the 54 uranyl peroxide clusters reported, 50 are cages built from uranyl hexagonal bipyramids in which two or three of the equatorial edges correspond to peroxide ligands.[1f] Three uranyl peroxide clusters, U20R, U24R, and U32R, have wheel-shaped structures, but these contain five and six-membered rings of uranyl polyhedra, and their topologies are

very different from *{U₂₀V₂₀}*.[1f] Recently, six uranyl peroxide cage clusters that contain tungstate or molybdate polyhedra within their cage walls have been reported, but these generally feature structural units consistent with uranyl peroxide clusters, and the transition metal polyhedra are simply linkers between uranyl ions.[14] The wheel-shaped *{U₆W₁₅}* cluster contains dimers of uranyl ions in hexagonal bipyramids bridged through bidentate peroxide, and five-membered units of molybdate square pyramids and octahedra.[15]

{U₂₀V₂₀} contains 10 tridentate sulfate tetrahedra that are likely essential for stability. The sulfate is derived from the ethyl sulfate and/or added H_2SO_4 or $VOSO_4$. Reduction of the pH below 4.0 by adding additional H_2SO_4 crystallized *{V₁₀}* decavanadate rather than *{U₂₀V₂₀}*. The ionic liquid provided *EMIm* cations that did not template cluster formation, but that were needed for crystallization. Na cations may have assumed a structure-directing role that encouraged closure of the wheel, but more likely they were simply opportunistic in finding suitable coordination environments within the cluster.

Although many uranyl vanadate compounds are known, several of which contain carnotite or francevillite-type sheets,[16] the polyhedral connectivity exhibited by *{U₂₀V₂₀}* is unique. Indeed, the formation of *{U₂₀V₂₀}* rather than an extended carnotite-type structure containing Na was not a predictable outcome of the synthesis reaction.[16f] In *{U₂₀V₂₀}* sulfate, or some other tetrahedral oxyanion, is likely necessary to stabilize the wheel structure, but in the absence of sulfate, *{U₂V₁₆}* formed rather than carnotite-type sheets. Carnotite-group compounds have low aqueous solubility, and the simple combination of reactants in water, in the absence of 3-Ethyl-1-methylimidazolium ethyl sulfate ionic liquid, would have immediately formed a solid precipitate due to hydrolysis. In experiments where *{U₂₀V₂₀}* or *{U₂V₁₆}* crystallized, uranyl nitrate was first dissolved in the ionic liquid which is only poorly miscible in water, which was in turn layered with or mixed with water containing sodium and vanadate. Attempts to synthesize *{U₂₀V₂₀}* using other ionic liquids containing the imidazolium cation, but with bistriflimide or diethyl phosphate anions, were unsuccessful. Although the details remain unclear and will be the subject of future work, dissolving the uranyl in the ionic liquid prior to mixing with water results in the slow crystallization of *{U₂₀V₂₀}* or *{U₂V₁₆}*.
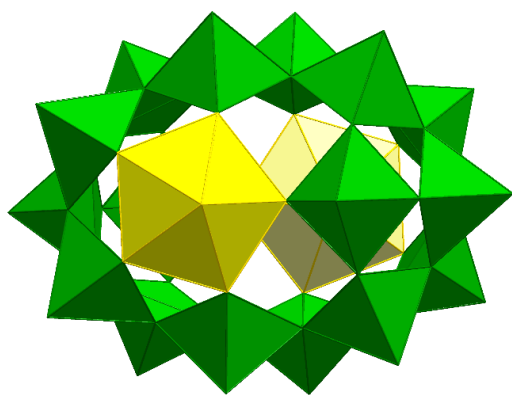
Figure 4. The *{U₂V₁₆}* cluster in **2** formed from two uranyl pentagonal bypyramids (yellow) and 16 vanadate square pyramids (green).

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