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Synthesis and Structure of $Ag_6[(UO_2)_3O(MoO_4)_5]$: A Novel Sheet of Triuranyl Clusters and MoO_4 Tetrahedra

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The new uranyl molybdate $Ag_6[(UO_2)_3O(MoO_4)_5]$ (**1**) with an unprecedented uranyl molybdate sheet has been synthesized at 650 °C. The structure (monoclinic, $C2/c$, $a = 16.4508(14)$ Å, $b = 11.3236(14)$ Å, $c = 12.4718(13)$ Å, $\beta = 100.014(4)^\circ$, $V = 2337.4(4)$ Å^3, $Z = 4$) contains $[(UO_2)_3O(MoO_4)_5]$ sheets composed of triuranyl $[(UO_2)_3O]$ clusters that are connected by MoO_4 tetrahedra. The topology of the uranyl molybdate sheet in **1** represents a major departure from sheets observed in other uranyl compounds. Of the ∼120 known inorganic uranyl compounds containing sheets of polyhedra, **1** is the only structure that contains trimers of uranyl pentagonal bipyramids that are connected only by the sharing of vertexes with other polyhedra. The sheets are parallel to (001) and are linked by Ag cations.

Uranyl minerals and inorganic compounds have been extensively studied recently because of their importance for the long-term disposal of spent nuclear fuel and radioactive waste remediation.[1−3] Uranyl oxide hydrates,[4] phosphates,[5] silicates,[6] selenites,[7] iodates,[8] sulfates,[9] and molybdates[10] have been examined. Owing to the flexibility of the U−O−Mo linkages and the variety of U and Mo coordination polyhedra, uranyl molybdates display unusual structural complexity and variability. In our ongoing study of the structural chemistry of uranyl molybdates,[10c,f−l] we are exploring both hydrothermal and high-temperature procedures for preparation of compounds with novel structural topologies. We have found that alkali metal uranyl molybdate structures are topologically varied, ranging from finite clusters through chains and sheets to frameworks of uranyl and molybdate polyhedra. The size of the alkali metal cation is significant in determining the topology and geometrical shape of the associated uranyl molybdate unit. For example, $Na_6[(UO_2)(MoO_4)_4]$,[10g] $Rb_6[(UO_2)(MoO_4)_4]$,[10f] and $Cs_6[(UO_2)(MoO_4)_4]$[10i] are based upon topologically different types of uranyl molybdate finite clusters, and the Rb and Cs compounds are not isostructural. In addition, polymorphic varieties occur in alkali metal uranyl molybdates; the compound $Cs_2[(UO_2)_2(MoO_4)_3]$[10j] shows both three- (α) and two-dimensional (β) uranyl molybdate units. We are interested in the influence of other monovalent cations on the shape and dimensionality of uranyl molybdate structural units; thus Ag(I) was chosen because its relatively small size and unique coordination geometry could lead to novel structural moieties.

Hydrothermal synthesis using a mixture of $AgNO_3$, MoO_3, and $UO_2(CH_3COO)_2{\cdot}2H_2O$ gave yellow equant crystals of $Ag_2[(UO_2)_6(MoO_4)_7(H_2O)](H_2O)_2$. This compound is struc-

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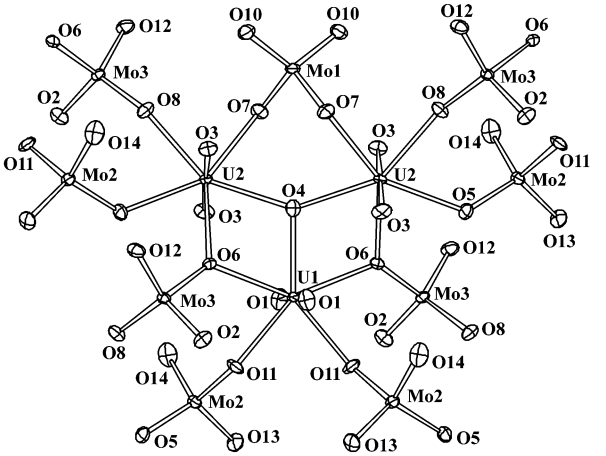

Figure 1. Triuranyl cluster surrounded by MoO_4 tetrahedra in the structure of $Ag_6[(UO_2)_3O(MoO_4)_5]$ (ellipsoids are drawn at 50% probability level).

turally similar to the series of framework compounds $M_2[(UO_2)_6(MoO_4)_7(H_2O)](H_2O)$ ($M = NH_4$, Cs,[10f] Rb[10k]), although its structural channels contain a different quantity of water.

Reaction of $AgNO_3$, UO_3, and MoO_3 for 5 h at 650 °C provided orange tabular transparent crystals of the new compound $Ag_6[(UO_2)_3O(MoO_4)_5]$ (**1**).[11]

The structure of **1**[12] contains novel sheets of UO_7 pentagonal bipyramids and MoO_4 tetrahedra. Three UO_7 pentagonal bipyramids form a triuranyl $[(UO_2)_3O_{11}]$ cluster by sharing the O(4) atom, which is not bonded to Mo (Figure 1). The O(4)−U bond lengths are in the range 2.262−2.361 Å, and the U−O−U angles are 108.0°, 108.0°, and 144.0°, which sum to 360° because the OU_3 moiety is planar. The $[(UO_2)_3O_{11}]$ clusters are linked into unprecedented sheets by sharing equatorial vertexes with MoO_4 tetrahedra (Figure 2a). Each MoO_4 tetrahedron is 2-connected; two O vertexes are shared with uranyl pentagonal bipyramids. The Mo−O distances for bridging O atoms are in the range 1.783−1.848 Å, whereas the Mo−O distances for terminal O atoms are 1.732−1.747 Å. This is in good agreement with previous results concerning the Mo−O bond lengths in the structures of uranyl molybdates. The uranyl molybdate sheets with composition $[(UO_2)_3O(MoO_4)_5]$ are parallel to (001) and are linked by Ag^+ cations coordinated by six (Ag(1) and Ag(3)) and five (Ag(2)) O atoms in irregular arrangements.

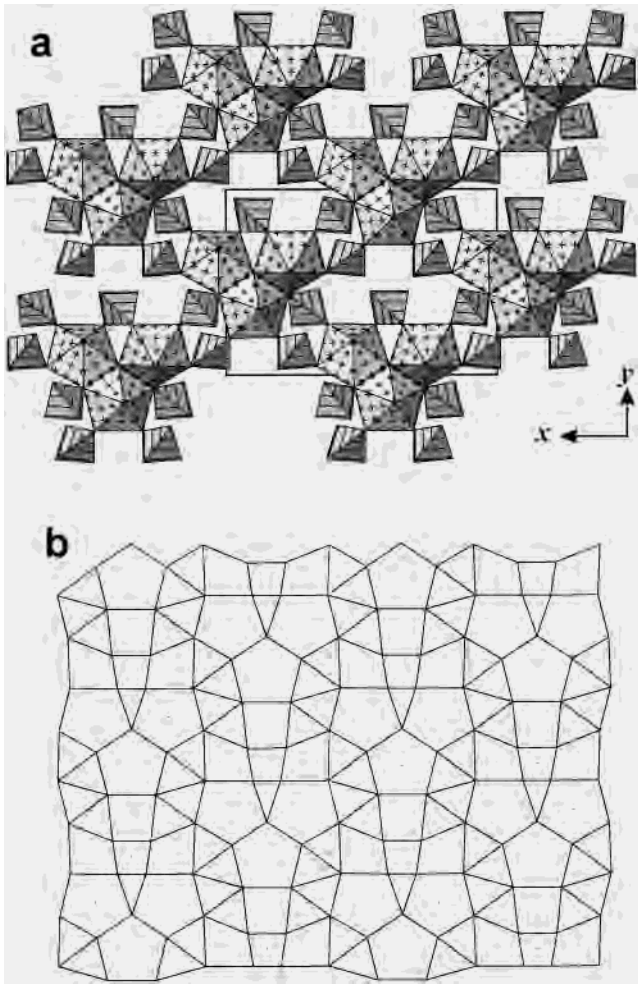

Figure 2. Polyhedral representation of the $[(UO_2)_3O(MoO_4)_5]$ sheet in the structure of $Ag_6[(UO_2)_3O(MoO_4)_5]$ (a) (legend: UO_7 polyhedra = shaded with crosses; MoO_4 tetrahedra = lined) and its anion topology (b).

Bond-valence sums for the cations, calculated using parameters for U(VI)−O,[14,15] Mo(VI)−O,[16] and Ag(I)−O[16] bonds are 6.07, 5.91, 5.80, 5.88, 5.71, 0.89, 0.77, and 0.92 vu (valence units) for U(1), U(2), Mo(1), Mo(2), Mo(3), Ag(1), Ag(2), and Ag(3), respectively. Bond-valence sums of the O atoms range from 1.78 to 2.22 vu.

The UO_7 pentagonal bipyramids and MoO_4 tetrahedra are relatively rigid structural components, in comparison with the interpolyhedral linkages. The $O_{eq}-U-O_{eq}$ and $O_{Ur}-U-O_{eq}$ bond angles (O_{Ur} = O atom of a uranyl ion; O_{eq} = equatorial O atom) are in the range 67.7−79.9° (ideally 72°) and 82.6−99.0° (ideally 90°), respectively, and the O−Mo−O angles are in the range 105.5−115.2° (ideally 109.5°). In contrast, the Mo−O−U bond angles vary from 119.8° to 155.2°, demonstrating that these interpolyhedral linkages are rather flexible. This observation is consistent with uranyl molybdates in general; thus they are potential candidates for displaying highly anisotropic thermal expansion and contraction.

Burns et al.[13] developed a structural hierarchy of inorganic uranyl compounds that is based upon the polymerization of polyhedra of high bond valence. Owing to the uneven

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(11) $Ag_6[(UO_2)_3O(MoO_4)_5]$ (**1**) was prepared by loading $AgNO_3$ (0.068 g), MoO_3 (0.058 g), and UO_3 (0.057 g) into a platinum crucible. The mixture was at 650 °C for 5 h in air, following by cooling to 300 °C over 50 h and then to 50 °C over 10 h. The product consisted of orange tabular transparent crystals of **1**, as well as a few dark red crystals of $Ag_{10}[(UO_2)_8Mo_5O_{28}]$, the structure of which will be reported elsewhere.

(12) Crystallographic data for $Ag_6[(UO_2)_3O(MoO_4)_5]$ (**1**): monoclinic, $C2/c$, $a = 16.4508(14)$ Å, $b = 11.3236(14)$ Å, $c = 12.4718(13)$ Å, $\beta = 100.014(4)^o$, $V = 2337.4(4)$ Å^3, $Z = 4$; crystal dimensions: 0.20 × 0.18 × 0.05 mm; $\rho_{calcd} = 6.46$ g·cm^{-3}, $\mu = 282.94$ cm^{-1}. Data collection: Bruker SMART APEX CCD diffractometer, 12852 total reflections, 4771 unique reflections, 3791 unique reflections $|F_o| \geq 4\sigma_F$. The structure solved by direct methods and refined to R1 = 0.054, wR2 = 0.105, $S = 0.984$ (anisotropic displacement parameters for all atoms).

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distribution of bond valences within uranyl polyhedra,[14] polymerization results in the formation of sheets in more than 60% of known structures. Uranyl polyhedra most often share equatorial polyhedral elements with other uranyl polyhedra, resulting in infinite chains that are linked to form sheets. Less commonly, uranyl polyhedra do not share vertexes, but are linked into sheets by sharing polyhedral elements with other cation polyhedra. The latter is common in uranyl molybdates, in which uranyl pentagonal bipyramids are often linked by the sharing of vertexes with molybdate tetrahedra. Sheets containing finite clusters of uranyl polyhedra are very rare; isolated dimers of edge-sharing uranyl pentagonal bipyramids occur in the sheets of vandenbrandeite, $[(UO_2)Cu(OH)_4]$, johannite, $Cu[(UO_2)_2(SO_4)_2(OH)_2](H_2O)_8$, and the synthetic compound $Sr[(UO_2)_2(SO_4)_2(OH)_2](H_2O)_8$,[13] and clusters within sheets that contain more than two uranyl polyhedra have not been reported. The topology of the uranyl molybdate sheet in **1** thus represents a major departure from sheets observed in other inorganic uranyl compounds. Of the ∼120 known structures of inorganic uranyl compounds containing sheets, it is the only one that contains trimers of uranyl polyhedra that are linked via sharing vertexes with other cation polyhedra. We hypothesize that the unusual connectivity of the sheet in **1** is related to the small size of Ag^+ in the interlayer; further investigations of Ag^+ uranyl compounds are underway to determine if additional unique structural topologies exist in these phases.

Consideration of the topological arrangement of anions within the $[(UO_2)_3O(MoO_4)_5]$ sheet[13,14] permits comparison with other sheet structures of inorganic uranyl compounds. The sheet anion topology is obtained by removing all cations and any 1-connected anions from consideration. The anions in the plane of the sheet separated by less than ∼3.5 Å are joined by lines. Projection of the sheet anion topology results in a two-dimensional tiling of space that ideally reflects packing of anions within the plane of the sheet. The anion topology of the $[(UO_2)_3O(MoO_4)_5]$ sheet in the structure of **1** is shown in Figure 2b. It consists of pentagons, squares, and triangles. In the sheet, all of the pentagons are populated by U, and $^1/_4$ of the squares and $^1/_2$ of the triangles contain Mo. Comparison to the sheet anion topologies for uranyl compounds given by Burns et al.[13] and Burns[14] demonstrates that this topology is novel.

Table 1. Selected Bond Distances (Å) for $Ag_6[(UO_2)_3O(MoO_4)_5]$ (**1**)

U(1)−O(1)[a]	1.818(6)	Mo(3)−O(2)	1.733(6)
U(1)−O(1)	1.818(6)	Mo(3)−O(12)	1.747(6)
U(1)−O(4)	2.262(8)	Mo(3)−O(8)	1.783(5)
U(1)−O(11)[b]	2.313(5)	Mo(3)−O(6)	1.848(6)
U(1)−O(11)[c]	2.313(5)	Ag(1)−O(2)[f]	2.346(6)
U(1)−O(6)	2.381(5)	Ag(1)−O(13)[g]	2.410(6)
U(1)−O(6)[a]	2.381(5)	Ag(1)−O(13)[a]	2.475(6)
U(2)−O(9)	1.794(6)	Ag(1)−O(10)	2.534(6)
U(2)−O(3)	1.811(6)	Ag(1)−O(12)[g]	2.697(6)
U(2)−O(7)	2.336(6)	Ag(1)−O(11)	2.759(6)
U(2)−O(4)	2.361(3)	Ag(2)−O(12)[h]	2.354(6)
U(2)−O(6)[a]	2.368(5)	Ag(2)−O(14)[i]	2.448(7)
U(2)−O(8)[d]	2.370(5)	Ag(2)−O(10)[j]	2.517(6)
U(2)−O(5)[e]	2.376(5)	Ag(2)−O(3)[k]	2.587(6)
Mo(1)−O(10)	1.734(6)	Ag(2)−O(5)[j]	2.680(6)
Mo(1)−O(10)[a]	1.734(6)	Ag(3)−O(1)[l]	2.247(6)
Mo(1)−O(7)[a]	1.811(6)	Ag(3)−O(3)[a]	2.284(5)
Mo(1)−O(7)	1.811(6)	Ag(3)−O(9)[l]	2.565(6)
Mo(2)−O(14)	1.732(6)	Ag(3)−O(14)[g]	2.701(7)
Mo(2)−O(13)	1.736(6)	Ag(3)−O(7)	2.757(6)
Mo(2)−O(11)	1.789(5)	Ag(3)−O(4)	2.883(2)
Mo(2)−O(5)	1.806(6)		

[a] $-x + 1, y, -z + {}^1/_2$. [b] $x, y + 1, z$. [c] $-x + 1, y + 1, -z + {}^1/_2$. [d] $x + {}^1/_2, y - {}^1/_2, z$. [e] $x + {}^1/_2, y + {}^1/_2, z$. [f] $x, y - 1, z$. [g] $x, -y - 1, z - {}^1/_2$. [h] $-x + {}^1/_2, y - {}^1/_2, -z + {}^1/_2$. [i] $-x + {}^1/_2, -y - {}^3/_2, -z + 1$. [j] $x, -y - 1, z + {}^1/_2$. [k] $-x + 1, -y - 1, -z + 1$. [l] $-x + 1, -y, -z$.

The current study further demonstrates the high degree of flexibility and structural variability of uranyl molybdate units that permits response to changing cation size and coordination geometry. In uranyl molybdates prepared by hydrothermal routes, no oxide anions are shared between UO_n polyhedra only. In contrast, in compounds synthesized at high temperatures in the absence of water, sharing of O atoms between U polyhedra only is common (compounds $M_6[(UO_2)_2O(MoO_4)_4]$ (M = Na,[10g] K,[10g] Rb[10k]) and $Cs_4[(UO_2)_3Mo_3O_{14}]$[10i]).

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Supporting Information Available: A file of X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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