

Uranium(VI) Adopts a Tetraoxido Core

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The hydrothermal reaction of uranyl acetate with cadmium acetate, or the high-temperature solid state reaction of arsenic(V) oxide, barium nitrate, and uranyl nitrate results in the formation of $\text{Cd}_2(\text{H}_2\text{O})_2[\text{U}(\text{OH})(\text{CH}_3\text{COO})(\text{UO}_2)_5(\text{OH})_2\text{O}_8] \cdot 0.5\text{H}_2\text{O}$ (**1**) or $\text{Ba}_4[(\text{UO}_2)_7(\text{UO}_4)(\text{AsO}_4)_2\text{O}_7]$ (**2**), respectively.

Both of these compounds contain uranium sites whose bonding metrics are consistent with the coordination environments found for Np^{VII} and Pu^{VII} not U^{VI} .

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Introduction

At the heart of uranium coordination chemistry is the *trans* dioxido cation uranyl, UO_2^{2+} , known for U^{VI} for many decades.^[1] This concept was recently challenged with the report of a *cis*- UO_2^{2+} unit,^[2] but this work proved to be spurious,^[3] and variations in the *trans* dioxido cation remain elusive. Transuranium elements can exceed the maximum oxidation state of VI for uranium, and well-characterized examples of actinides in the heptavalent oxidation state are known for neptunium^[4] and plutonium.^[5] A transient octavalent Pu species may also exist in basic media.^[6] In most of these examples the An^{VII} ($\text{An} = \text{Np}, \text{Pu}$) ion is found as a six-coordinate tetragonal bipyramid with an approximately planar tetraoxido core.^[7] This coordination environment is unique to the actinides. One can basically think of the An^{VII} cation as the inverse of the U^{VI} cation. For An^{VII} there are two long and four short bonds in a molecule like $[\text{NpO}_4(\text{OH})_2]^{3-}$. For An^{VI} there are four long and two short bonds in a tetragonal bipyramidal arrange-

ment (e.g. in $[\text{UO}_2(\text{OH})_4]^{2-}$). Herein we report that U^{VI} can also adopt a tetraoxido core similar to that found for Np^{VII} and Pu^{VII} .

Results and Discussion

The hydrothermal reaction of uranyl acetate with cadmium acetate, or the high-temperature solid-state reaction of arsenic(V) oxide, barium nitrate, and uranyl nitrate results in the formation of brown crystals of $\text{Cd}_2(\text{H}_2\text{O})_2[\text{U}(\text{OH})(\text{CH}_3\text{COO})(\text{UO}_2)_5(\text{OH})_2\text{O}_8] \cdot 0.5\text{H}_2\text{O}$ (**1**) in 21% yield as a pure phase and dark red crystals of $\text{Ba}_4[(\text{UO}_2)_7(\text{UO}_4)(\text{AsO}_4)_2\text{O}_7]$ (**2**) formed in excess of arsenic oxides, respectively. The color of these crystals is abnormal; typical uranyl compounds containing these constituents should be yellow.

These investigators were quite concerned given the unusual bonding in these compounds that something (e.g. twinning or incorrect unit cell) was wrong with the initial structure. Single crystal X-ray diffraction experiments were performed on three different crystals. All data sets converged to the same structure with low residuals. These studies revealed a complex layered cadmium uranyl oxyhydroxide acetate and a three-dimensional framework barium uranium arsenate, shown in parts a and b of Figure 1. The topology of these phases quite similar, and we start with the description of the simpler phase **1**.

 $\text{Cd}_2(\text{H}_2\text{O})_2[\text{U}(\text{OH})(\text{CH}_3\text{COO})(\text{UO}_2)_5(\text{OH})_2\text{O}_8] \cdot 0.5\text{H}_2\text{O}$

The topology of **1** is very similar to that of the mixed-valent $\text{U}^{\text{V}}/\text{U}^{\text{VI}}$ compound, $[\text{U}^{\text{V}}(\text{H}_2\text{O})_2(\text{U}^{\text{VI}}\text{O}_2)_2\text{O}_4(\text{OH})] \cdot (\text{H}_2\text{O})_4$, whose structure and spectroscopic details were recently reported by Cahill and co-workers.^[8] However, in **1** there are six crystallographically unique uranium sites. Four

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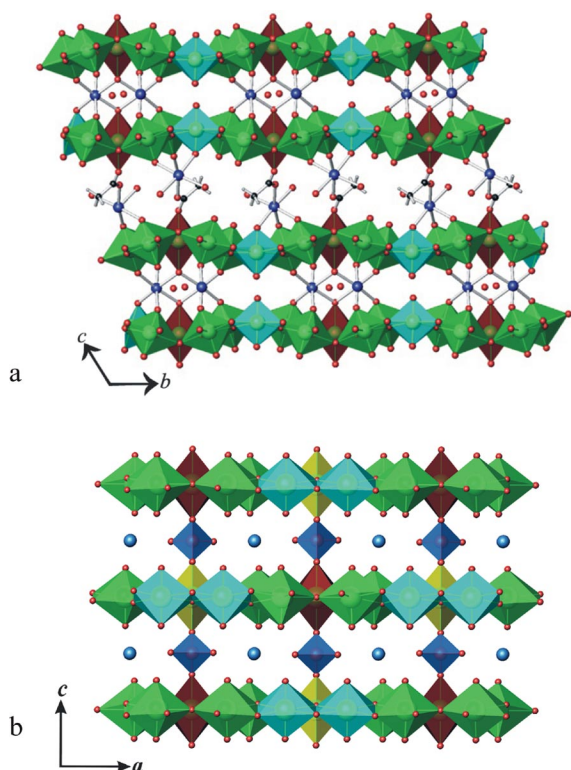


Figure 1. General views of the structures of **1** and **2** showing uranyl oxyhydroxide (**1**) and uranyl oxido layers (**2**) joined together by acetate and Cd^{2+} cations (blue) in **1**, and oxoarsenate groups and Ba^{2+} cations in **2**. UO_7 pentagonal bipyramids are shown in green and UO_6 tetragonal bipyramids are shown in light blue, yellow, and brown.

of these sites yield normal UO_7 pentagonal bipyramids with standard uranyl cores. The average $\text{U}=\text{O}$ bond in these uranyl moieties is 1.827(8) Å.

The fifth site is a typical UO_6 tetragonal bipyramid with an average $\text{U}=\text{O}$ bond length of 1.814(8) Å. There is a second UO_6 site that is the focus of this discussion that will be expanded upon later. It should be noted that there is direct coordination between some of the uranyl oxido atoms and the Cd^{2+} cations. The UO_7 and UO_6 polyhedra combine to form a layered substructure, depicted in Figure 2 (a), where the two-dimensional features are linked by the Cd^{2+} cations.

As can be seen in this latter Figure, there is no *trans* dioxido cation. The two *trans* bonds where the uranyl cation would normally be located have been replaced by two much longer $\text{U}-\text{O}$ bonds of 2.306(8) and 2.340(7) Å. The first of these is to a bridging acetate anion that links U(1) and Cd(1). The second is to an oxygen atom that we are speculating is actually a hydroxide group. The remaining four short equatorial $\text{U}-\text{O}$ bonds range from 1.961(7) to 2.000(7) Å. These bonding metrics are consistent with the coordination environments found for Np^{VII} and Pu^{VII} not U^{VI} .^[4b,5,7] The key features of the structure of **1** and **2** are the tetragonal bipyramids that are depicted in Figure 1 (a) and Figure 2 (a) in brown, and expanded on in Figure 3 to show the local coordination environment for **1**.

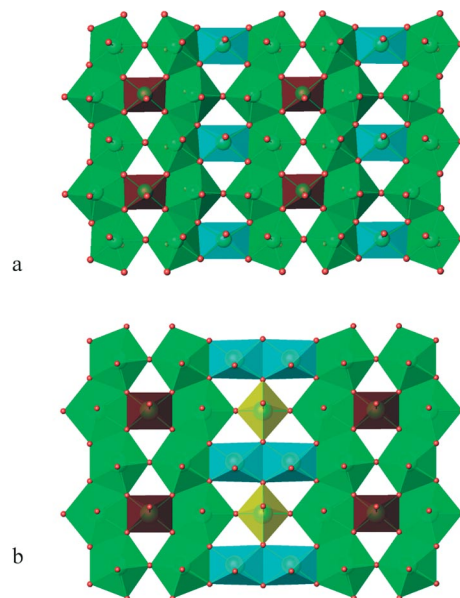


Figure 2. Views of part of one of the layers in **1** (a) and **2** (b).

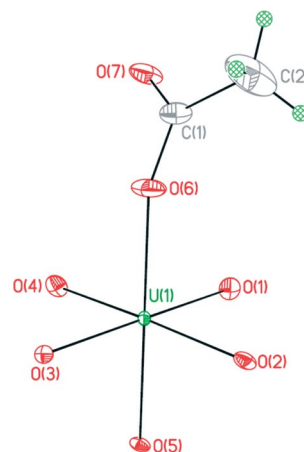


Figure 3. A view of the local coordination environment around U(1) in **1** showing two long axial $\text{U}-\text{O}$ bonds to O(5) and O(6) averaging 2.323(8) Å and four short equatorial $\text{U}-\text{O}$ bonds to O(1)–O(4) averaging 1.987(7) Å.

$\text{Ba}_4[(\text{UO}_2)_7(\text{UO}_4)(\text{AsO}_4)_2\text{O}_7]$

The structure of **2** is based on sheets linked into a 3D framework by AsO_4 tetrahedra as it is visible from Figure 1 (b). The topology of 2D sheets in **2** is similar with the topology of layers in **1** (Figure 2, b). We can see that additional fragments in **2** are two types of tetragonal bipyramids, UO_6 . The first one is same as in **1** (polyhedra printed in blue), and here there are uranyl groups directed perpendicular to layers plane. The second type is different (polyhedra printed in yellow). Here the uranyl groups are parallel to the layers. The UO_4 groups are found in same positions as in **1** (polyhedra printed in brown). All distances in the equatorial plane of these bipyramids are identical and equal to 2.021(8) Å, which is very close to the bond lengths in **1**. The axial bonds $\text{U}-\text{O}$ in these polyhedra are shorter than in **1**.

at 2.26(1) Å. In **2** these ligands are oxoarsenate groups AsO_4 , which are symmetrically coordinated to the UO_4^{2-} group as is shown in Figure 4 (a).

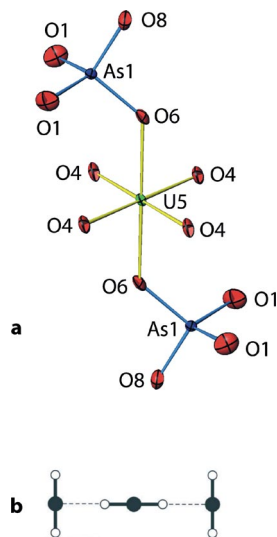


Figure 4. a. A view of the local coordination environment around U(5) in **2** showing two long axial U–O bonds to O(6) and four short equatorial U=O bonds to O(4) with lengths of 2.021(8) Å. b. Schematic representation of cation–cation interactions geometry in **2**.

The uranyl groups $\text{U}(4)\text{O}_2^{2+}$ (polyhedra, yellow) in the structure of **2** are coordinated by two uranyl groups $\text{U}(1)\text{O}_2^{2+}$ and form a new geometry of cation–cation interactions. This trimer is schematically presented in Figure 4 (b), and is an isomer of the trimer previously observed in $\text{Li}_2(\text{UO}_2)_4(\text{WO}_4)_4\text{O}_3$,^[9] and eight recognized types of cation–cation interactions in uranyl compounds.^[10]

General Aspects

While it is not possible for uranium to obtain an oxidation state higher than +6, lower oxidation states are readily available. If the sheet topology of $[\text{U}^{\text{V}}(\text{H}_2\text{O})_2(\text{U}^{\text{VI}}\text{O}_2)_2\text{O}_4(\text{OH})](\text{H}_2\text{O})_4$ is adopted as a model, the U(1) in **1** and U(5) in **2** sites would be the ones that contain U^{V} . However, bond-valence sum calculations yield a value of 6.00 for this site, which is consistent with the proposed +6 oxidation state.^[1] As expected, all of the bonds to U(1) in **1** and U(5) in **2** are notably shorter than those found for the U^{V} site in $[\text{U}^{\text{V}}(\text{H}_2\text{O})_2(\text{U}^{\text{VI}}\text{O}_2)_2\text{O}_4(\text{OH})](\text{H}_2\text{O})_4$.^[8] The remaining five sites also have bond-valence sums consistent with U^{VI} . The high negative charge that this moiety bears is compensated for by coordination of the tetraoxido core to six neighboring uranyl cations as shown in Figure 2 (a, b). It should be noted that the structure of the U(1) site in **1** and U(5) site in **2** are inconsistent with theory that predicted that $\text{U}^{\text{VI}}\text{O}_4^{2-}$ would possess a tetrahedral geometry.^[11] The general configuration of axial coordination of UO_4 groups in both synthesized phases can be presented in $\text{L}^{n-}\text{--UO}_4^{2-}\text{--L}^{n-}$ form; here a variety of ligands can occupy these sites (e.g., OH^- , AsO_4^{3-} , and CH_3COO^-).

Bond-valence sum calculations can only suggest formal oxidation states, and as previously stated, the colors of these compounds are inconsistent with simple U^{VI} compounds. The most obvious source of the dark colorations is partial reduction of one of more of the uranium sites to U^{V} . Magnetic susceptibility measurements were carried out to test for this on **1**, because it can be prepared in pure form. The effective moment, determined from the fits assuming a single U site contribution, is $0.40(5)\mu_{\text{B}}$, a value much smaller than the free ion value of $2.54\mu_{\text{B}}$ expected for U^{5+} (an $5f^1$ system) assuming Russell–Saunders coupling, but much larger than the solely diamagnetic response expected for a uranyl(VI) ion under the same coupling scheme. Excited-state contributions to a measured moment through a configuration mixing mechanism are unlikely at the low temperatures over which the data were obtained.^[12] Effective moments near the free-ion value have previously been measured for U^{5+} in a site with dioxido coordination.^[13] There are also reports of significantly reduced effective moments of about $0.9\text{--}1.3\mu_{\text{B}}$ measured in ternary fluorite structures^[14] and $0.50\text{--}0.66\mu_{\text{B}}$ in ternary perovskite phases.^[15] Uranyl in the fluorite structure has four equatorial oxygen atoms, whereas the perovskite phase has uranium in a distorted octahedron. Thus, the magnetism rules out a simple uranyl(VI) compound but it is not clear whether the moment is generated by a intermediate-valent uranyl or a U^{5+} ion with an effective moment that appears to be sensitive to the crystal field. In summary, the magnetic and optical responses are consistent with the presence of some U^{5+} in **1**.

Conclusions

It should be noted that similar UO_4 groups have been previously observed in simple uranates (complex oxides),^[16] where all oxygen atoms are bridging between uranium sites. Here we show that this site is much more flexible, and that different ligands can occupy the axial positions. **1** and **2** are examples of uranium compounds containing a site that adopts a geometry that is more consistent with the heptavalent states found for Np and Pu.

Experimental Section

$\text{Cd}_2(\text{H}_2\text{O})_2[\text{U}(\text{OH})(\text{CH}_3\text{COO})(\text{UO}_2)_5(\text{OH})_2\text{O}_8]\cdot 0.5\text{H}_2\text{O}$ (1**):** Uranyl acetate (210 mg, 0.495 mmol) was treated with cadmium acetate (175 mg, 0.657 mmol) in 1 mL of H_2O at 180 °C for three days in a PTFE-lined autoclave, followed by slow cooling to room temperature over 24 h.

Crystal Structure Determination: Brown needle, crystal dimensions $0.130 \times 0.038 \times 0.012$ mm, triclinic, $P\bar{1}$, $Z = 2$, $a = 7.0681(6)$, $b = 11.5215(9)$, $c = 15.1306(12)$ Å, $\alpha = 107.230(1)^\circ$, $\beta = 97.964(1)^\circ$, $\gamma = 90.017(1)^\circ$, $V = 1164.40(16)$ Å³ ($T = 296$ K), $\mu = 434.58$ cm^{−1}, $R_1 = 0.0302$, $wR_2 = 0.0861$. Bruker APEX CCD diffractometer: $\theta_{\text{max}} = 57.48^\circ$, Mo- K_{α} , $\lambda = 0.71073$ Å, $0.3^\circ \omega$ scans, 14016 reflections measured, 5538 independent reflections all of which were included in the refinement.

Ba₄[(UO₂)₇(UO₄)(AsO₄)₂O₇] (2): Uranyl nitrate, arsenic(V) oxide and barium nitrate were taken in molar ratio 3:3:1. Mixture was grounded in agate mortar, placed in a platinum crucible and heated to 1150 °C with following slow cooling (7 °C/h). Crystals of **2** formed in excess of arsenic oxide as dark-red agglomerates.

Crystal Structure Determination: Dark-red plate, crystal dimensions 0.23 × 0.12 × 0.01 mm, orthorhombic, *Pmna*, *Z* = 2, *a* = 15.535(1), *b* = 7.0420(10), *c* = 14.0940(10) Å, *V* = 1541.8(3) Å³ (*T* = 296 K), *μ* = 490.99 cm⁻¹, *R*₁ = 0.0424, *wR*₂ = 0.1171. Mar300 Image Plate diffractometer: *θ*_{max} = 56.02°, Mo-*K*_α, *λ* = 0.71073 Å, 1° *φ* scans, 12868 reflections measured, 1813 independent reflections all of which were included in the refinement.

All crystal data was corrected for Lorentz-polarization effects and for absorption, structures were solved by direct methods, anisotropic refinement of *F*² by full-matrix least-squares.^[17] Further details of the crystal structure investigations may be obtained from the Fachinformationzentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (crysdata@fiz-karlsruhe.de) on quoting numbers CSD-420762 (for **1**) and CSD-420763 (for **2**).

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