

## Structural Characterization of the First Hydroxo-Bridged Plutonium Compound, $(\text{PuO}_2)_2(\text{IO}_3)(\mu_2\text{-OH})_3$

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Received May 11, 2005

The hydrothermal reaction of a  $^{239}\text{Pu}(\text{IV})$  stock solution in the presence of iodic acid and 1 M KOH produces reddish-brown single crystals of  $(\text{PuO}_2)_2(\text{IO}_3)(\text{OH})_3$ . The structure consists of two-dimensional layers forming in the *ac* plane and is the first single-crystal structure of plutonium(VI) connected through hydroxide anions. The additional linkage of plutonium centers is completed through iodate ligands.

The chemical and structural similarities among the light actinide elements (Th, U, Np, Pu, Am, Cm) in a given oxidation state have been the focus of intense research and application for decades. Oxidation state analogies have provided the ability to study the chemical behavior of easily accessible actinides, such as thorium(IV) and uranium(VI), and to use their compounds' structural, thermodynamic, and kinetic properties to model and guide the chemistries of more difficult-to-handle actinides, such as plutonium.<sup>1</sup> In fact, the ability of plutonium to exist in aqueous environments in multiple oxidation states (III, IV, V, and VI) simultaneously creates a highly dynamic system that encompasses the different oxidation state-dependent chemistries and redox properties.<sup>2</sup> To predict the diverse complexation chemistry of plutonium ions in aqueous solutions, the structural and thermodynamic data of analogous compounds with actinides in more stable oxidation states (Am(III), Th(IV), Np(V), or U(VI)) has been utilized.

Although this oxidation state analogy was applied successfully to assess the chemistry of plutonium in very diverse media, such as carbonate, hydroxide, fluoride, and chloride, the chemical and structural differences between uranium(VI) and plutonium(VI) have been of historical discussion. As an example, at near-neutral pH U(VI) tends to form polynuclear hydroxo species, e.g.  $(\text{UO}_2)_2(\text{CO}_3)(\text{OH})_3^-$  or  $(\text{UO}_2)_3(\text{OH})_5^+$ , when the U(VI) concentration in solution rises

above approximately  $10^{-4}$  mol/L.<sup>3</sup> In carbonate solutions, the trimeric U(VI) species,  $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$  has been observed and its structural and thermodynamic properties determined.<sup>3,4</sup> In these polynuclear complexes, uranyl(VI) polyhedra are linked together by bridging  $\mu_2\text{-OH}^-$ ,  $\mu_3\text{-O}^{2-}$ , or  $\mu_2\text{-CO}_3^{2-}$  groups. Under similar conditions, plutonium(VI) seems to prefer to exist as mononuclear solution complexes. Although some polynuclear Pu(VI) hydroxo complexes have been suggested to exist in solution,<sup>5</sup> the absence of any structural information does not corroborate with this claim. In fact, the directed synthesis and crystallization efforts of polynuclear Pu(VI) species from aqueous solutions have been unsuccessful, and consequently, the structural information of Pu(VI) hydroxo compounds remains absent. A similar gap on crystallographic data exists for hydroxo compounds of plutonium in its III, IV, and V oxidation states.

In our efforts to synthesize<sup>6</sup> and structurally characterize<sup>7</sup> plutonium compounds, we were able to obtain single crystals of the mixed Pu(VI) hydroxo–iodate compound,  $(\text{PuO}_2)_2(\text{IO}_3)(\text{OH})_3$  (**1**). The structure of the binary Pu(VI) iodate,  $\text{PuO}_2(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$  (**2**),<sup>8</sup> has been reported as forming under hydrothermal conditions at pH = 0 and is the first example of a solid-state plutonium(VI) single-crystal structure. To target a Pu(VI) hydroxide compound, a stock

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- (6) (**1**):  $\text{H}_2\text{IO}_6$  (44.2 mg, 0.21 mmol) was loaded in a 10-mL PTFE-lined autoclave followed by 0.5 mL of  $\text{H}_2\text{O}$  and 100  $\mu\text{L}$  of  $^{239}\text{Pu}(\text{IV})$  stock solution. The pH was adjusted to 5 using 700  $\mu\text{L}$  of 1 M KOH. The autoclave was sealed, doubly contained in two heat-sealed Teflon bags, and placed in box furnace preheated to 200°C. After 48 h, the furnace was cooled at 13 °C/h to 25 °C. Product consisted of colorless solution over reddish-brown rectangular plate single crystals. CAUTION: Plutonium-239 is a highly radioactive element, and standard precautions for handling radioactive materials should be followed.

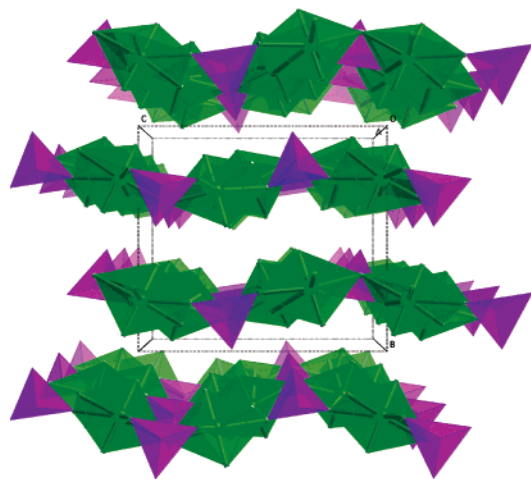
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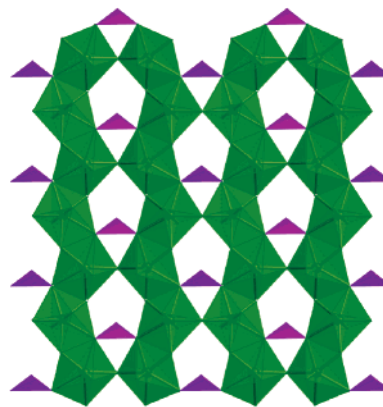


**Figure 1.** Packing of plutonyl(VI) polyhedra (green) and iodate pyramids (purple) of **1** illustrating the arrangement of layers and the alignment of the terminal iodate oxygen atoms toward adjacent layers (view down the *a* axis).

solution of Pu(IV) was reacted with hydroxide in the presence of

$\text{H}_5\text{IO}_6$  at 200 °C for 48 h. The high oxidation potential of the periodate anion ( $E^\circ(\text{IO}_4^-/\text{IO}_3^-) = 1.65 \text{ V}^9$ ) was used to oxidize Pu(IV) completely to the hexavalent oxidation state ( $E^\circ(\text{Pu}^{4+}/\text{PuO}_2^{2+}) = 0.98 \text{ V}^5$ ). Thin, red-brown, rectangular crystals formed with nearly quantitative removal of plutonium from solution; no Pu(VI) peak in the solution absorbance spectrum was observed after the reaction. The X-ray crystal structure analysis revealed the crystalline product to be  $(\text{PuO}_2)_2(\text{IO}_3)(\text{OH})_3$ . This is the first plutonium hydroxo compound to be structurally characterized that contains bridging hydroxo groups as a principal structural component.

Compound **1** is a two-dimensional structure built from corner- and edge-sharing  $[\text{PuO}_7]$  and  $[\text{IO}_3]$  units. Two crystallographically unique plutonium atoms are linked to form infinite chains down the *a* axis, as shown in Figure 1. Iodate and hydroxo groups connect the chains, forming infinite layers in the *ac* plane. The slightly distorted



**Figure 2.** View of the infinite two-dimensional sheets that run down the *a* axis. Plutonium chains are formed from edge-sharing  $[\text{PuO}_7]$  polyhedra (green), which are linked by bridging  $\text{IO}_3$  (purple) and OH ligands.

**Table 1.** Selected Interatomic Distances (Å) and Bond Angles (deg)

Pu1–O5	1.759(9)	Pu2–O6	1.746(10)	Pu1–Pu2	3.9175(10)
Pu1–O4	1.771(11)	Pu2–O7	1.748(10)	Pu1–Pu2	3.9352(10)
Pu1–O8	2.277(9)	Pu2–O8	2.308(9)	I1–O1	1.769(10)
Pu1–O9	2.379(9)	Pu2–O9	2.342(9)	I1–O3	1.845(11)
Pu1–O10	2.380(8)	Pu2–O10	2.390(9)	I1–O2	1.890(10)
Pu1–O3	2.461(11)	Pu2–O2	2.459(10)		
Pu1–O2	2.569(12)	Pu2–O3	2.577(10)		
O5–Pu1–O4	178.0(4)	O1–I1–O2	99.9(5)		
O6–Pu2–O7	179.1(4)	O3–I1–O2	100.1(5)		
O1–I1–O3	99.3(4)				

pentagonal bipyramidal  $[\text{PuO}_7]$  polyhedra are comprised of two axial trans-oxygen ( $\text{O}=\text{Pu}=\text{O}$ ) atoms and five oxygen atoms in the equatorial plane. Two  $\text{O}_{\text{eq}}$  atoms derive from two monodentate coordinated  $[\text{IO}_3]$  units, while bridging  $[\text{OH}]$  ligands provide the remaining three  $\text{O}_{\text{eq}}$  atoms. The average  $\text{Pu}=\text{O}$  bond length of 1.76(1) Å and the  $\text{O}=\text{Pu}=\text{O}$  bond angles of 178.0(4)° for Pu(1) and 179.1(4)° for Pu(2) compare well with those found in **2** (1.75(1) Å and 178.9(4)°)<sup>8</sup> or in the  $\text{PuO}_2^{2+}$  aquo ion (1.74(1) Å)<sup>10</sup> determined by X-ray absorption spectroscopy. Selected bond lengths and bond angles are presented in Table 1. The intense diffuse reflectance band at 837 nm, characteristic for Pu(VI), confirmed the oxidation state of plutonium.

The pyramidal  $\text{IO}_3^-$  anions assist in joining adjacent chains of  $[\text{PuO}_7]$  polyhedra, as depicted in Figure 2. Each  $[\text{IO}_3]$  group joins four plutonium atoms through two  $\mu_3$ -oxygen atoms with one remaining terminal oxygen atom that is arranged along the *c* axis and pointing toward the adjacent plutonyl iodate sheets. The iodine atoms form trigonal pyramids slightly distorted from  $3m$  symmetry, with three I–O bond lengths ranging between 1.77(1) (terminal O) and 1.89(1) Å and O–I–O angles of 99.3(4)°, 99.9(5)°, and 100.1(5)°, which are within the expected range for  $\text{IO}_3^-$  groups.<sup>9,11</sup> In addition, there are two weak  $\text{I}\cdots\text{O}$  interactions at longer distances (2.50–2.63 Å), as also found in other transition metal<sup>12,13</sup> and lanthanide iodates.<sup>14,15</sup> A

(7) Crystal data for  $(\text{PuO}_2)_2(\text{IO}_3)(\text{OH})_3$ :  $M = 767.90$ ,  $P2_1/n$ ,  $a = 7.164(2)$  Å,  $b = 10.520(3)$  Å,  $c = 11.561(3)$  Å,  $\beta = 90.179(5)^\circ$ ,  $V = 871.3(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calcd}} = 5.876 \text{ g/cm}^3$ ,  $\mu(\text{Mo K}\alpha) = 185.71 \text{ cm}^{-1}$ ,  $T = -70$  °C,  $R_1 = 0.0388$ ,  $wR_2 = 0.1268$ . Crystals of  $(\text{PuO}_2)_2(\text{IO}_3)(\text{OH})_3$  ( $0.04 \times 0.08 \times 0.12 \text{ mm}^3$ ) were mounted in glass capillaries after being coated with epoxy. The capillaries were then coated with clear nail polish as a third form of containment. Triple containment is necessitated by the associated health hazards of working with plutonium. Data were collected on a Bruker P4 with Smart 1K CCD X-ray diffractometer using a Bruker LT-2 low-temperature device. Data were collected using a sealed, graphite monochromatic Mo K $\alpha$  X-ray source. A hemisphere of data was collected using a combination of  $\varphi$  and  $\omega$  scans, with 30-s frame exposures and 0.3° frame widths. Data collection, initial indexing, and cell refinement were handled using SMART software. Frame integration and final cell parameter calculations were carried out using SAINT software. The data were corrected for absorption using SADABS. The program suite SHELXTL was used for space group determination (XPREP), structure solution (XS), and refinement (XL). The final refinement included anisotropic displacement parameters for all nonhydrogen atoms. Hydrogen atom positions were not included in the structure refinement. The number of hydrogen atoms in the compound formula is consistent with charge balance, bond distances, and angle criteria for hydroxy groups.

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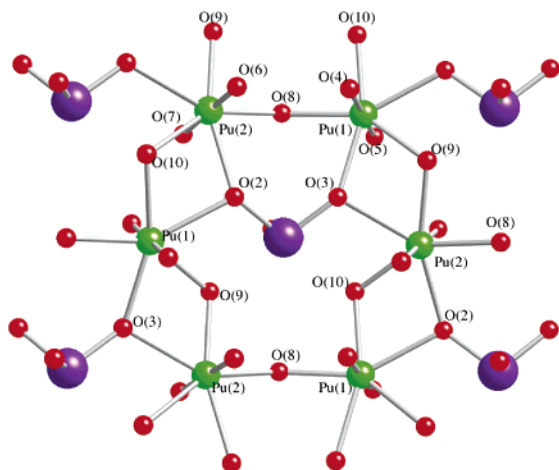
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**Figure 3.** Assembly of six plutonium atoms (green) that are connected via bridging  $\text{IO}_3^-$  and  $\text{OH}^-$  anions (I, purple; O, red). The  $\mu_2\text{-O(9)H}$  groups bridge the Pu atoms within the chain along the  $a$  axis; the chains are linked by  $\mu_2\text{-O(8)H}$  and  $[\text{IO}_3^-]$  groups.

distant plutonyl oxygen atom at 3.65 Å completes a pseudo-octahedral geometry of six oxygen atoms around the iodine atom. The Pu–OIO<sub>2</sub> distances of 2.46(1) and 2.57(1) Å in the equatorial plane are slightly longer than those found in **2** (2.332(7)–2.418(8) Å) or with analogous U–OIO<sub>2</sub> bond distances reported in U(VI) iodate compounds (2.421(9) Å).

The most interesting feature of this structure is the connection of plutonium atoms by hydroxide and iodate groups. Each bridging oxygen atom from the iodate group shares two plutonium atoms, which results in the coordination of four metal centers by only two iodate oxygen atoms. In addition, bridging hydroxo anions, which are to date uncharacterized for Pu(VI) compounds, connect the  $[\text{PuO}_7]$  polyhedra. The Pu–OH distances in the equatorial plane that are associated with the  $\mu_2\text{-OH}$  (O(9) and O(10)) ligand in the edge-sharing intrachain linkage range between 2.342(9) and 2.390(9) Å. The shortest Pu–O distances of 2.277(9) (Pu(1)) and 2.308(9) Å (Pu(2)) correlate to the O(8) atom of the corner-sharing  $[\text{PuO}_7]$  polyhedra of adjacent chains, found in Figure 3.

The coordination chemistry of uranyl(VI) hydroxide/oxide compounds is based on the assembly of tetra-, penta-, or hexagonal U(VI) polyhedra that are linked by bridging  $\mu_2\text{-hydroxo}$  or  $\mu_3\text{-oxo}$  groups. The uranyl polyhedra are generally completed by four, five, or six ligands in the

equatorial plane around the linear  $(\text{O}=\text{U}=\text{O})^{2+}$  moiety.<sup>16</sup> In the dimeric hydrolysis product,  $(\text{UO}_2)_2(\text{OH})_2^{2+}$ , two bridging hydroxo groups link two uranium atoms. With subsequent addition of  $(\text{O}=\text{U}=\text{O})^{2+}$  dioxo cations,  $\mu_2\text{-O}$  atoms stabilize higher assemblies of  $(\text{O}=\text{U}=\text{O})^{2+}$  units, as found in the trimeric  $(\text{UO}_2)_3(\text{OH})_5^+$  or the tetranuclear species  $[(\text{UO}_2)_4(\mu_3\text{-O})_2(\mu_2\text{-OH})_4(\text{H}_2\text{O})_6]$ . Similar observations have been found in extended U(VI) structures, which allowed the systematic classification of U(VI) minerals and inorganic phases on the basis of polymerized uranyl polyhedra.<sup>16</sup> Although polynuclear plutonyl(VI) hydroxo species have been proposed to exist and thermodynamic stability constants have been determined,<sup>5</sup> the bridging nature of Pu atoms by  $\mu_2\text{-OH}$  ligands has not been found in any structurally characterized plutonium compound. The presence of  $\mu_2\text{-OH}$  groups in **1** illustrates that Pu(VI) displays a rich coordination chemistry, which is comparable to U(VI). However, differences in the stability of structural features are obvious as noted in the different structures of the binary U(VI) and Pu(VI) iodates,  $\text{UO}_2(\text{IO}_3)_2\cdot\text{H}_2\text{O}$  and  $\text{PuO}_2(\text{IO}_3)_2\cdot\text{H}_2\text{O}$ , respectively.<sup>17</sup> The arrangement of  $\mu_2\text{-OH}$  and  $\mu_2\text{-IO}_3$  ligands bridging the Pu centers in **1** is unprecedented in lanthanide and actinide iodates. As another example, in the U(VI)–iodato–chloro–hydroxo compound,  $\text{Cs}_2[(\text{UO}_2)_3\text{Cl}_2(\text{IO}_3)(\text{OH})\text{O}_2]\cdot 2\text{H}_2\text{O}$ ,<sup>18</sup> iodate is bridging only two uranium atoms and  $\mu_3\text{-O}$  groups are the centers of triangular uranyl(VI) clusters. The inclusion of  $\mu_3\text{-O}$  groups remains an unknown architecture in Pu(VI) hydroxide or oxide compounds. However, compound **1** brings us one step closer to confirm that the structural features of U(VI) prevail in Pu(VI) compounds.

**Acknowledgment.** This work was supported by the Department of Energy, the LANL postdoctoral program, and the Pu Stabilization and Scrap Recovery Program (Project leader Dr. Paul H. Smith) at Los Alamos National Laboratory. Los Alamos National Laboratory is operated by the University of California for the U. S. Department of Energy under Contract No. W-7405-ENG-36.

**Supporting Information Available:** X-ray crystallographic files for  $(\text{PuO}_2)_2(\text{IO}_3)(\text{OH})_3$  in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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