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Structural characterization of the first hydrothermally synthesized plutonium compound, $PuO_2(IO_3)_2{\cdot}H_2O$

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Received (in Purdue, IN, USA) 8th November 2002, Accepted 12th December 2002
First published as an Advance Article on the web 16th January 2003

DOI: 10.1039/b211018k

Single crystals of $PuO_2(IO_3)_2{\cdot}H_2O$ were synthesized under hydrothermal conditions (180 °C) representing the first structurally characterized transuranium iodate.

The iodate anion, IO_3^-, forms a large class of inorganic structures with transition metals[1–4] and lanthanides[5–10] that are of broad interest due to their diverse coordination chemistries, magnetic properties at low temperatures, and as model materials to investigate hydrogen bonding in hydrated iodate compounds. While common oxo-anionic compounds of hexavalent actinides, *i.e.* SO_4^{2-}, CO_3^{2-}, NO_3^-, PO_4^{3-}, are highly soluble in acidic media, iodate offers the unique capability to precipitate actinides even under mildly acidic conditions.[11,12] In fact, iodate precipitation was used for oxidation state determination of plutonium in October 1942.[13] Plutonium(IV) was precipitated from HNO_3 solutions upon addition of HIO_3[13] or KIO_3;[12] however, the exact compositions of the precipitates remain unknown.[12] The calculated molecular weight did not match the suggested formula, $Pu(IO_3)_4$, indicating the possible presence of KIO_3 or HIO_3 in the solid. While no Pu(V) and Pu(VI) iodates are known, there are reports on the preparation of U(VI), Np(V) and Np(VI) iodates. In particular, brownish-yellow $NpO_2(IO_3)_2{\cdot}2H_2O$ and $[Co(NH_3)_6](NpO_2)_2(IO_3)_7{\cdot}7H_2O$ were precipitated by excess of KIO_3.[11] Despite the isolation and partial spectroscopic characterization of neptunium and plutonium iodates, the actinide oxidation state and structural information of these compounds are still deficient. More recently, the single crystal structures of a varied assortment of uranyl(VI) iodates have been reported.[14]

We report herein the synthesis and structural characterization of the binary plutonium(VI) iodate, $PuO_2(IO_3)_2{\cdot}H_2O$ (**I**), and compare its structural features with those of the chemically analogous compound, $UO_2(IO_3)_2H_2O$ (**II**).[14b] Although hydrothermal conditions have been applied to the synthesis of transition metal, lanthanide and uranium compounds, the transuranium elements (neptunium, plutonium) were largely excluded from this approach because of safety and contamination concerns. We reacted Pu(IV) or Pu(VI) with KIO_4 in 0.5 M HCl solutions at 180 °C for 24 h.† The high oxidation potential of the periodate anion in acid ($E°(IO_4^-/IO_3^-)$ = 1.65 V[15]) oxidizes Pu(IV) completely to the hexavalent state ($E°(Pu^{4+}/PuO_2^{2+})$ = 0.98 V[16]). In both cases, red rectangular crystals formed with nearly quantitative removal of plutonium from solution. The X-ray crystal structure analysis revealed the crystalline product to be $PuO_2(IO_3)_2{\cdot}H_2O$.‡ This is the first transuranium iodate compound to be structurally characterized and also the first overall reported single crystal structure of a compound containing the PuO_2^{2+} cation.

The structure of **I** consists of infinite staggered layers lying down the crystallographic *ab* plane with water molecules arranged between the layers (Fig. 1). The layers are built from corner-sharing $[IO_3]$ and $[PuO_7]$ units. The plutonium $[PuO_7]$ polyhedra are comprised of two *trans*-oxygen atoms with an O=Pu=O angle of 178.9(4)° and five $[IO_3]$ oxygens atoms in the equatorial plane to complete a slightly distorted pentagonal-bipyramidal coordination. The averaged Pu=O bond length of 1.75(1) Å compares well with those found by XAS for other Pu(VI) compounds, such as 1.74(1) Å in the PuO_2^{2+} aquo ion[17] and in $(K\text{-}18\text{-crown-}6)_2PuO_2Cl_4$.[18] The oxidation state of plutonium was confirmed by the characteristic peak of Pu(VI) at about 830 nm in the diffuse reflectance and in the absorbance spectrum of **I** when dissolved in $HClO_4$. The Pu–O distances in the equatorial plane range between 2.332(7) Å and 2.418(8) Å which are similar to those observed in reported U(VI) iodate compounds.[14]

Two crystallographically distinct pyramidal IO_3^- anions bridge the plutonium atoms (Fig. 2). The $[I(1)O_3]$ groups join two plutonium atoms with one remaining terminal oxygen atom, O(6), which is arranged along the *c* axis and points towards an adjacent plutonyl iodate sheet. The bond lengths of 1.807(6) Å for I(1)–O(5) and 1.808(8) Å for I(1)–O(6) as well as the angles including the terminal oxygen, 99.7(3)° for O(5)–I(1)–O(6) and 97.5(4)° for O(4)–I(1)–O(6), are within the expected range for IO_3^- groups.[14] However, the $[I(1)O_3]$ geometry is distorted due to a slightly longer I(1)–O(4) bond of 1.844(7) Å and a significantly smaller angle between the two coordinating oxygens, 91.9(3)° for O(4)–I(1)–O(5). The distortion in the $[I(1)O_3]$ groups also shortens the distance between the μ_2-oxygen atoms in the pyramidal plane, O(4) and O(5), to 2.62 Å. In contrast, the $[I(2)O_3]$ units coordinate three plutonyl units and exhibit expected nearly symmetric I–O bond lengths and angles, *i.e.* the averaged I–O bond is 1.81(1) Å and the averaged O–I(2)–O angle is 97(1)°. The averaged oxygen–oxygen distance of 2.73(3) Å in the pyramidal plane of $[I(2)O_3]$ compares well with the 2.72(6) Å found for the O–O distances in the iodate groups in **II**. A close contact between I(2) and the terminal oxygen of the $[I(1)O_3]$ group, O(6), at a longer distance of about 2.72 Å is found. This longer interaction between the μ_2- and μ_3-iodate groups compares well with those found in **II** (2.67–2.87 Å[14]), but is significantly longer than those found in the anhydrous $UO_2(IO_3)_2$ (2.49 Å[14]), the $Sc(IO_3)_3$ (2.56 Å [10]), or other iodate-bearing compounds such as $KIO_3{\cdot}HIO_3$ (2.35 and 2.56 Å[19]). The water molecules are arranged below the

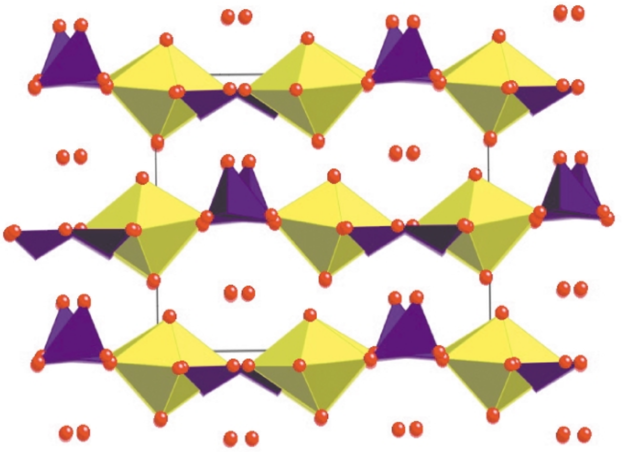
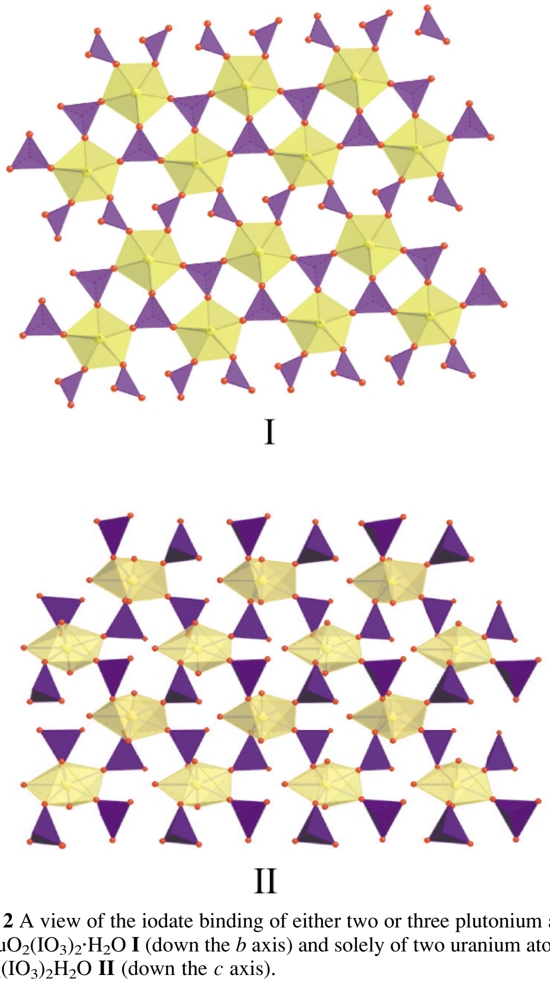


Fig. 1 Packing of plutonyl polyhedra and iodate pyramids of **I** (view down the *a* axis) illustrating the arrangement of layers and lattice waters.

[I(1)O_3] plane with a distance I(1)–O(1W) of 2.69 Å and in line with the I(1)–O(6) bond.

Each plutonium atom is bridged by five iodate ligands to six other Pu atoms. Monodentate linkage of two metal centers by one iodate has been previously observed in U(VI) iodates[14] and is also known in lanthanide[9,10] and transition metal iodates.[2,3] However, coordination of three metal centers by all three oxygen atoms of the IO_3^- anion, as observed in this compound, has only been found in trivalent lanthanide iodate compounds.[7] The different coordination of iodate groups is manifested in their Raman spectra. As expected, the plutonyl(VI) frequency for **I** is observed at 856 cm^{-1} reflecting a weaker Pu=O bonding than in U=O (1.782 Å,[14] 880 cm^{-1}). The different coordination modes and the distortion of the [I(1)O_3] group in **I** result in a change in the Raman spectrum with the main stretching frequencies of the iodate anion at 803, 785 (most intense), and 746 cm^{-1}.

Structural characterization of plutonium complexes is rare and mainly focuses on the reduced oxidation states of Pu(III) and Pu(IV). Only a few complexes of Pu(VI) with oxo-anions have been characterized by powder X-ray diffraction or X-ray absorption spectroscopy. Most plutonyl(VI) complexes are tetra- (*i.e.* PuO_2Cl_4) or hexa-coordinate (*i.e.* $PuO_2(CO_3)_3^{4-}$) in the equatorial plane. Compound **I** is the first plutonyl(VI) complex with pentagonal coordination (beside the $PuO_2(H_2O)_5^{2+}$ aquo ion[17]) as is also found in the uranyl(VI) analogue, $UO_2(IO_3)_2H_2O$ (**II**). However, the latter is built up from [UO_7] polyhedra where one water molecule is directly coordinated to a uranium atom (U–O_W = 2.458(5) Å); four iodate oxygens complete the pentagonal-bipyramidal coordination around the uranyl axis (Fig. 2). The inner-coordination of one water molecule to uranium induces the O=U=O units to angle towards one another causing corrugated layers, while the linear O=Pu=O moieties are parallel within the flat layers in compound **I**. The iodate groups in **II** solely bridge two uranium centers, whereas in **I**, iodate bridging of two and three plutonium atoms occurs. Bidentate chelation of IO_3^-, as found in anhydrous $UO_2(IO_3)_2$,[14] is absent in both hydrated iodates **I** and **II**.



I

II

Fig. 2 A view of the iodate binding of either two or three plutonium atoms in $PuO_2(IO_3)_2{\cdot}H_2O$ **I** (down the *b* axis) and solely of two uranium atoms in $UO_2(IO_3)_2H_2O$ **II** (down the *c* axis).

Under hydrothermal conditions we could reliably obtain good quality crystals of plutonyl iodate using KIO_4 and Pu(IV) or Pu(VI). Synthesis under ambient conditions yielded microcrystalline or amorphous precipitates. Using other iodate-based starting materials, such as I_2O_5 or KIO_3, resulted in the formation of microcrystalline Pu(VI) iodate or a mixture of Pu(IV) and Pu(VI) precipitates. It will be of interest if we are able to synthesize neptunium iodates and study which of the binding modes that were found in U(VI) and Pu(VI) iodates will prevail. Although this synthesis did not resolve the structural uncertainties regarding the Pu(IV) precipitate from 1942, our present efforts focus on the synthesis of Pu(IV) iodate.

Notes and references

† Hydrothermal reactions were performed in 10 mL PTFE-lined Parr autoclaves, which were loaded with 200 microliters of either ^{239}Pu(IV) or ^{239}Pu(VI) stock solution (0.17 M in 1 M HCl), 74 mg KIO_4 and 800 microliters of deionized water. The vessels were heated at 180 °C for 1 day, then ramp cooled at 13 °C h^{-1}.

‡ *Crystal data* for $PuO_2(IO_3)_2{\cdot}H_2O$: $H_2I_2O_9Pu$, M = 638.82, orthorhombic, $Pn2_1a$, a = 7.320(1), b = 9.473(1), c = 11.636(2) Å, V = 806.8(2) Å^3, T = 203 K, Z = 4, λ(Mo-Kα) = 1.6 mm^{-1}, 3786 reflections measured, 1139 unique (R_{int} = 0.028) which were used in all calculations. The final $wR(F^2)$ was 0.044 (all data). CCDC reference number 197636. See http://www.rsc.org/suppdata/cc/b2/b211018k/ for crystallographic data in CIF or other electronic format.

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