Title
Characterization of a mixed salt of 1-hydroxy-pyridin-2-one Pu(IV) complexes

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Authors
Gorden, Anne E.V.
Xu, Jide
Szigethy, Geza
et al.

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Most expert analyses of the projected world energy needs show utilization of nuclear energy will be essential for the next few decades, and hence the need to support this technology grows. But as one measure of the supporting science base of this field, as of December 2006, only 25 Pu containing structures were in the Cambridge Structural Database, as compared to 21,807 for Fe.\(^2\) A comparison of the rate of addition to this knowledge base reveals that approximately 500 Fe structures are registered with the Cambridge Structural Database every year, while in the same period only two or three Pu crystal structures are published.

A continuing objective of this laboratory has been the development of new sequestering agents for actinide decorporation and selective extractions. This effort has been based on similarities in the properties of Pu(IV) and Fe(III), and the chelating groups in microbial Fe(III) sequestering agents, siderophores.\(^3\) The HOPO ligands (Figure 1) are one such class of chelating group which have been investigated as selective actinide extractants.\(^4\)\(^-\)\(^7\).

We previously reported the first hydroxypyridonate Pu(IV) complex structure, the tetradentate 5LIO(Me-3,2-HOPO) ligand with Pu(IV).\(^8\) Here, we report a new structure of the bidentate 1,2-HOPO ligand with Pu(IV). Although a slight excess of ligand to metal was used (1:4.1 M:L ratio), the tetrakis(bidentate) structure did not form exclusively; one Pu is complexed by four 1,2-HOPO ligands, while the other is complexed by three ligands and two water molecules. Due to the small size of the crystals and safe handling considerations for working with Pu, the solid-state structure was determined by X-ray diffraction using synchrotron radiation from beamline 11.3.1 at the Advanced Light Source (ALS). The use of synchrotron radiation has been found to be of great benefit with crystals that might not yield high quality data sets using a traditional laboratory radiation source.\(^9\)\(^-\)\(^11\) The crystals of the Pu-(1,2-HOPO) complex form as black block-like crystals from acidic aqueous solution. The crystal conforms to space group \(\text{P}2_1\) with \(Z=2\).\(^12\)\(^-\)\(^13\) The asymmetric unit contains two independent, eight-coordinate plutonium complexes and one disordered perchlorate anion (Figure 2).\(^14\) One complex is the tris(bidentate) complex \([\text{Pu}(1,2\text{-HOPO})_3(\text{H}_2\text{O})_2\text{ClO}_4]\) with a Pu(IV) atom coordinated by three 1,2-HOPO ligands and two water molecules. The other complex is the expected tetrakis complex \([\text{Pu}(1,2\text{-HOPO})_4]\) with the Pu(IV) cation coordinated by the eight oxygens of four 1,2-HOPO ligands. The crystal exists as a racemic twin with a ratio of 48:52. The perchlorate ion is disordered and has been modeled with four oxygens distributed over eight positions.

![Figure 1](image1.png)

**Figure 1.** (a) 1-Hydroxy-pyridin-2-one (1,2-HOPO) and (b) 3-hydroxy-N-methyl-pyridin-2-one (Me-3,2-HOPO).

There are two different Pu-HOPO bond types in these complexes: those with the N-hydroxamate oxygens and those with the carbonyl oxygens. The average Pu-O(N-hydroxamate) bond distance for the tetrakis complex (Pu2) is the same as that for the Pu-O(carbonyl) bonds at 2.33(2) Å. The average Pu-O bond distances in the M:L = 1:3 complex (Pu1) have similar values, with the Pu-O(N-hydroxamate) bond distances averaging 2.31(1) Å and the Pu-O(carbonyl) distances averaging 2.30(2) Å. As with the tetrakis complex, these bond distances are equal, within their standard deviations. Equality of M-O distances is also seen in the Fe(III)-1,2-HOPO complex, and is ascribed to the aromatization of the heteroatom ring.\(^16\) Approximate M-O bond equality was also observed in the previously-reported Pu-5LIO-Me-3,2-HOPO structure in which the average Pu-O(phenolic) bond distance was 2.28(4) Å whereas the average Pu-O(amide) distance was 2.38(4) Å.\(^8\) Bond length equality is usually characteristic of square antiprismatic (\(D_{4d}\)) geometry, but shape analysis\(^17\) shows that one molecule in the Pu-(1,2-HOPO) crystal most closely resembles a bicapped trigonal prism (\(C_{2v}\)), while the other approaches trigonal dodecahedral geometry (\(D_{2d}\)). The difference between the shape measures for the bicapped trigonal prism (\(C_{2v}\)) and trigonal dodecahedral (\(D_{2d}\)) geometries for both Pu-(1,2-HOPO) species does not exceed 2.3°, so they appear to have an intermediate geometry between the two. Aromatization of the HOPO ring is most likely the cause of the intermediate
coordination geometries exhibited in the Pu-(1,2-HOPO) complexes which lie between C2v and D3d geometries, both of which require M-O bond inequality.

Due to its similar charge-to-radius ratio and solution chemistry, Ce(IV) is often used as a structural model for Pu(IV). For comparison, the crystal structure of the previously-synthesized Ce(1,2-HOPO)4 complex was examined. The Ce(1,2-HOPO)4 structure closely resembles the [Pu(1,2-HOPO)4] complex; it crystallizes from acidic solution in the centrosymmetric space group P-1 with Z=2. Unlike the Pu crystal, the asymmetric unit contains two tetrakis(bidentate) (yet crystallographically unique) metal centers (Figure 3). According to shape analysis of these cerium complexes, the coordination geometry of both most closely resembles the trigonal dodecadhedron (D2d), although the difference between that and D3d geometry for one and C2v geometry for the other does not exceed 1.5°. This indicates that the coordination geometries of both are intermediates between high-symmetry geometries, as are their Pu analogs. The Ce-O bond lengths correlate well with the Pu-O distances; the average Ce-O(N-hydroxamate) distance is 2.33(2) Å and the average Ce-O(carbonyl) distance is 2.35(3) Å - almost exactly the same as the corresponding Pu-O bonds.

Figure 3. The asymmetric unit (ORTEP) of the Ce(IV)-(1,2-HOPO) crystal structure showing the two unique tetrakis(bidentate) complexes. Hydrogen atoms and solvent inclinations have been omitted for clarity.

Another interesting comparison to the Pu-1,2-HOPO complex is the crystal structure of the previously reported thorium(IV) complex, [Th(1,2-HOPO)3(H2O)]. In contrast to the eight-coordinate Pu(IV) and Ce(IV) structures, the larger Th(IV) is nine-coordinate, with a slightly distorted tricapped trigonal prismatic (D3h) coordination geometry. The M-O bonds are correspondingly longer in the Th(IV) complex; the average Th-O(N-coordinating) distance is 2.40 Å and the average Th-O(carbonyl) distance is 2.48 Å, which are between 0.05 Å and 0.20 Å longer than the corresponding Pu-O bonds in the Pu structures. The D3h coordination geometry, like the D3d geometry, does not require equal bond lengths, and the longer bond lengths in the Th(IV) structure are expected, since the Th(IV) cation is larger than either Ce(IV) or Pu(IV) and is nine-coordinate.

Ongoing studies include the characterization of the solution properties of these complexes by potentiometric and spectrophotometric titrations; other information fundamental to our understanding of the coordination chemistry and speciation of Pu(IV) complexes are needed in the development of actinide sequestering agents, waste treatment methods, and long-term strategies for nuclear waste repositories.

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Supporting Information Available: CIF files, crystallographic tables, summary bond-angle tables for the Ce(IV) and Pu(IV) crystal structures, and experimental preparations of plutonium stock solutions and plutonium crystals. This material is available free of charge via the Internet at http://pubs.acs.org.
A single crystal X-ray diffraction analysis of the mixed salt of hydroxypyridonate Pu(IV) complexes is presented; \([\text{Pu}(1,2\text{-HOPO})_3(\text{H}_2\text{O})_2\text{ClO}_4] \cdot \text{Pu}(1,2\text{-HOPO})_4\) crystallizes in \(P2_1\) with the asymmetric unit containing two distinct eight-coordinate Pu(IV) complexes, one tris(bidentate) and the other tetrakis(bidentate). The structure of this complex are compared to the analogous Ce(IV)- and Th(IV)-1,2-HOPO structures.