CHEMISTRY
A EUROPEAN JOURNAL

Sequestered Plutonium: [Pu^{IV}{5LIO(Me-3,2-HOPO)}$_2$]—The First Structurally Characterized Plutonium Hydroxypyridonate Complex**

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Abstract: The first single-crystal X-ray diffraction analysis of a hydroxypyridonate plutonium(IV) complex is presented, that of the tetradentate ligand 5LIO(Me-3,2-HOPO) with Pu^{IV}. The [Pu^{IV}{5LIO(Me-3,2-HOPO)}$_2$] complex crystallizes in the space group $Pna2_1$ with the asymmetric unit cell containing two unique eight-coordinate plutonium complexes and one perchlorate anion. According to shape measure analysis, the geometry of both Pu centers is closest to a bicapped trigonal prism (C_{2v} symmetry, for Pu1: $S(C_{2v}) = 13.48°$, $S(D_{4d}) = 15.43°$, $S(D_{4d}) = 16.10°$). The average bond length for the Pu–O(phenolic) is 2.31(4) Å, whereas the Pu–O(amide) distances are slightly longer, averaging 2.40(2) Å. The preparative chemistry of this compound and the implications of the structure are discussed.

Keywords: actinides · coordination chemistry · plutonium · structure elucidation

Introduction

The use of actinides in defense applications and energy production has resulted in environmental and health concerns and a legacy of environmental wastes.[1] As the world expands its needs for energy and seeks alternatives to fossil fuels, the challenge of limiting the potential environmental and health effects from contamination or exposure is increasing.[2] Complicating this problem is our relatively limited knowledge of the solution and coordination behavior of the actinides.[3]

Ligands for actinide decorporation and for extraction agents in waste remediation have been developed by using the hydroxypyridonate (HOPO) and catecholamide (CAM) chelating subunits found in siderophores, naturally occurring iron(III) sequestering agents.[1] The similar chemical properties and in vivo behavior of Pu^{IV} and Fe^{III} led to siderophore-based ligands for actinides designed to exploit these similarities.[4] Biological evaluation of the efficacy and toxicity of HOPO, CAM, and the related terephthalamide (TAM) ligands in mice has provided insight into the factors affecting the efficacy of a ligand for actinide chelation (e.g., denticity, binding group acidity, backbone flexibility, and solubility), enabling the development of improved actinide sequestering agents. Two HOPO-based ligands among these, tetradentate 5LIO(Me-3,2-HOPO) (**1**) and hexadentate TREN(Me-3,2-HOPO) (**2**) stand out as among the most effective for reducing the body content of Pu^{IV}, Am^{III}, Np^{V}–Np^{IV}, and U^{VI}, and are significantly more effective than CaNa$_3$-DTPA (DTPA = diethylenetriaminepentaacetic acid), the currently approved treatment for Pu, Am, and Cm.[1]

A detailed assessment of the structures of the actinide complexes formed is particularly important if new synthetic chelating ligands are to be designed for the selective coordination of actinide ions. As of this writing, only 23 plutonium complexes have been characterized by single-crystal X-ray diffraction and reported to the Cambridge Database, and many more will be required to generate a suitable framework for molecular modeling.[5–7] Here, we report the first structure of a hydroxypyridonate plutonium(IV) complex, that of the tetradentate 5LIO(Me-3,2-HOPO) (**1**) with Pu^{IV}. This also is the first Pu crystal structure determined by using a synchrotron radiation source for X-ray diffraction.

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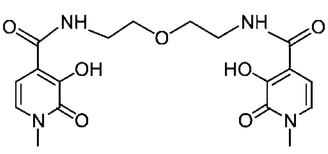
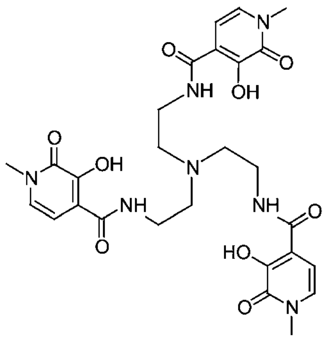
[**] Part 55 in the series "Specific Sequestering Agents for the Actinides." For Part 54, see: A. C. Veeck, D. J. White, D. W. Whisenhunt, Jr., J. Xu, A. E. V. Gorden, V. Romanovski, D. C. Hoffman, K. N. Raymond, *Solv. Extract. Ion Exch.* **2004**, *6*, 1037–1068

DOI: 10.1002/chem.200401193



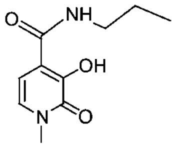
5LIO(Me-3,2-HOPO)

1



TREN(Me-3,2-HOPO)

2



PR(Me-3,2-HOPO)

3

Results and Discussion

Owing to the challenges of working with the radioactive actinides, lanthanides are often substituted as models for structural investigation. Cerium is the only lanthanide for which the +4 oxidation state is stable for several weeks in aqueous solutions,[3] and, in an eight-coordinate system, Ce^{IV} and Pu^{IV} are of similar ionic radii.[8] Because of this, Ce^{IV} has been used as a model for Pu^{IV}.[9,10] The tetradentate ligand 5LIO(Me-3,2-HOPO) (**1**) has been characterized in complexes with Ce^{IV} both as the [Ce{5LIO(Me-3,2-HOPO)}$_2$]·2 CH_3OH and [Ce{5LIO(Me-3,2-HOPO)}$_2$]·4 H_2O. In each case, the central Ce^{IV} atom forms an eight-coordinate sandwich-like complex with two tetradentate ligands.[11]

The Ce^{IV} complexes were prepared by adding cerium(IV) acetylacetonate in THF to a solution of the ligand in THF. After heating to reflux temperature overnight, the metal complex precipitated from the solution. This isolated precipitate was redissolved in chloroform, and after purification, crystals of [Ce{5LIO(Me-3,2-HOPO)}$_2$]·2 CH_3OH were grown by diffusing diethyl ether into a solution of the ligand in a mixture of methanol and chloroform. The crystals of the [Ce{5LIO(Me-3,2-HOPO)}$_2$]·4 H_2O complex were isolated from the atmospheric oxidation of [Ce^{III}{5LIO(Me-3,2-HOPO)}$_2$] prepared in a like manner, but crystallized from an aqueous solution.

This procedure provided the basis for the preparation of the Pu^{IV} complex. To limit the use of heat and organic solvents with the actinides, this complex was prepared by the addition of Pu^{IV} in 1.1 M $HClO_4$ to a solution of the ligand in water. Addition of the metal to the ligand causes the solution to change to an amber color. The crystals form as purple plates after the slow evaporation of the solvent. The final solution had a pH close to 2.

Owing to the small size of the crystals that would likely form from these materials and safe-handling considerations when working with Pu, the solid-state structure was determined by X-ray diffraction methods using synchrotron radiation from Beamline 11.3.1 at the Advanced Light Source (ALS) (Figure 1). This bending magnet Beamline provides an intense beam of monochromatic X-rays in the range 6–17 keV and can be used with crystals as small as 15 microns, ideal for this experiment. The use of a synchrotron radiation source has been found to be of great benefit with crystals that might not yield high quality data sets using traditional laboratory sources.[12–14]

The complex crystallizes in space group $Pna2_1$ with $Z=4$. Selected bond lengths and angles are given in Table 1. The asymmetric unit cell contains two unique eight-coordinate plutonium complexes and one disordered perchlorate anion. The two Pu-containing molecules are shown in relation to each other and the perchlorate ion in Figure 2. This minor amount of disorder is consistent with the conditions: the crystals were grown in water and the data collected at room temperature.

Each central Pu atom is coordinated by eight oxygen atoms, four each from two 5LIO(Me-3,2-HOPO) ligands,

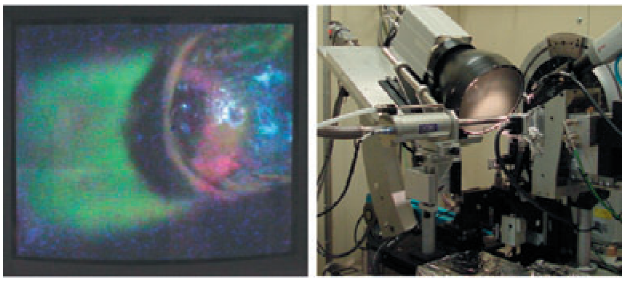


Figure 1. Left: Photograph of a crystal of the [Pu^{IV}{(5-LIO-Me-3,2-HOPO)}$_2$] complex under 20× magnification on the single-crystal diffractometer. Right: The small-molecule diffractometer at the Advanced Light Source.

Table 1. Selected bond lengths [Å] and angles [°] for the [Pu^{IV}{(5-LIO-Me-3,2-HOPO)}$_2$] complex for each of the unique molecules within the unit cell. Standard deviations for the last decimal place are given in parentheses.

phenolic oxygens		amide oxygens	
Pu1−O1	2.229(12)	Pu1−O2	2.397(11)
Pu1−O3	2.299(12)	Pu1−O4	2.410(10)
Pu1−O5	2.321(12)	Pu1−O6	2.371(12)
Pu1−O7	2.340(10)	Pu1−O8	2.425(10)
Pu2−O15	2.343(10)	Pu2−O16	2.427(11)
Pu2−O17	2.314(10)	Pu2−O18	2.386(10)
Pu2−O19	2.334(9)	Pu2−O20	2.397(10)
Pu2−O21	2.303(12)	Pu2−O22	2.386(13)
O1-Pu1-O2	66.8(4)	O1-Pu1-O7	134.2(4)
O3-Pu1-O4	66.5(4)	O2-Pu1-O8	135.1(4)
O5-Pu1-O6	67.6(4)	O3-Pu1-O5	131.8(5)
O7-Pu1-O8	67.5(4)	O6-Pu1-O4	133.5(4)
O15-Pu1-O16	67.9(4)	O21-Pu1-O15	133.0(4)
O17-Pu1-O18	67.0(4)	O22-Pu2-O16	133.7(4)
O19-Pu1-O20	67.2(4)	O18-Pu1-O20	136.5(4)
O21-Pu1-O22	67.5(4)	O17-Pu1-O19	134.4(4)

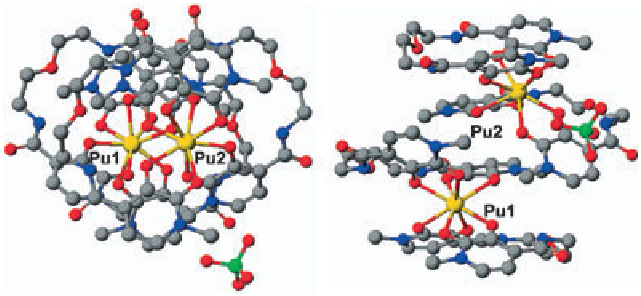


Figure 2. Unit cell system of the [Pu^{IV}\{5-LIO(Me-3,2-HOPO)\}$_2$] complex (generated from crystallographic data using CAChe) with two unique molecules and one perchlorate ion seen from the top (left) and side (C: gray; O: red; N: blue; Cl: green; Pu: yellow). The hydrogen atoms and water molecules have been omitted for clarity.

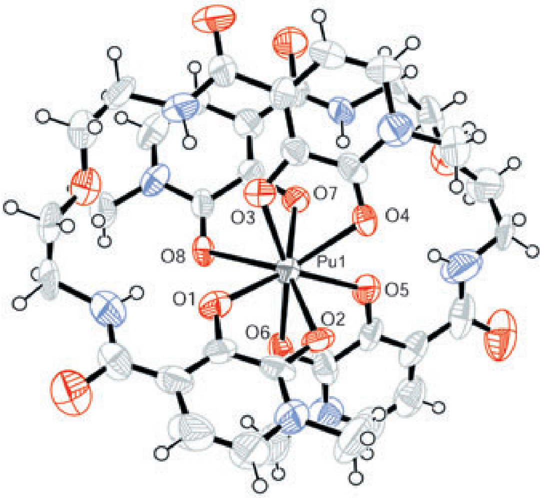


Figure 3. Molecular structure of [Pu^{IV}\{(5-LIO-Me-3,2-HOPO)\}$_2$] featuring the molecule about Pu1 (ORTEP plot, shown with the thermal ellipsoids (50% probability); C: light gray; O: red; N: blue; Pu: dark gray.

forming a sandwich-like structure (Figure 3). The planes of the HOPO chelating rings are bent at an angle to the plane defined by the amide ether linkage, the metal, and the HOPO oxygen atoms. This plane is represented in a schematic drawing shown in Figure 4. The overall ligand geometry about Pu1 more closely resembles a sandwich structure, while the ligands coordinating Pu2 are twisted just slightly more from planar. The average bite angle for each given hydroxypyridonate-chelating unit is 67.3(4)°.

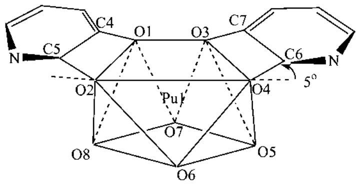


Figure 4. Schematic diagram using the idealized geometry of the Pu molecule from the side view. The plane of the sandwich structure is defined by the oxygen atoms coordinating to the plutonium center. The HOPO chelating units are tilted at an angle of 5° from this plane in Pu1. In this fashion, it resembles an open box, with the corners of the box defined by the oxygen atoms, and the lid by the planes of the HOPO rings.

There are two different types of coordinating oxygen bonds in each Pu molecule, the phenolic and amide oxygen atoms, with the oxygen atoms coordinating to the amide having a longer metal–oxygen bond length. For the Pu1 molecule, the average bond length for the Pu–O(phenolic) is 2.307(31) Å, whereas for Pu2 it is slightly longer, averaging 2.324(18) Å (Table 2). The differences in the Pu–O(amide) distances are negligible, averaging 2.401(23) Å for Pu1 and 2.399(19) Å for Pu2. The differences between the amide and phenolic bond lengths (0.094 Å for Pu1 and 0.075 Å for Pu2), are comparable to that of methanolic and aqueous Ce^{IV} complexes (0.116 and 0.111 Å, respectively). This illustrates some of the limits of Ce^{IV} as a structural model.

Table 2. Median, mean, and standard deviations of corresponding bond lengths from each of the [Pu^{IV}\{(5-LIO-Me-3,2-HOPO)\}$_2$] molecules within the unit cell and for each of the reported [Ce^{IV}\{(5-LIO-Me-3,2-HOPO)\}$_2$] complexes.

	Pu1 bond lengths [Å]		Pu2 bond lengths [Å]	
	phenolic oxygens	amide oxygens	phenolic oxygens	amide oxygens
average	2.307	2.401	2.324	2.399
median	2.310	2.404	2.324	2.392
standard deviation	0.031	0.023	0.018	0.019
	Ce in H_2O bond lengths [Å]		Ce in MeOH bond lengths [Å]	
	phenolic oxygens	amide oxygens	phenolic oxygens	amide oxygens
average	2.293	2.409	2.296	2.407
median	2.292	2.410	2.298	2.292
standard deviation	0.015	0.018	0.012	0.015

The unit cell also contains five water molecules, three of which are modeled as six half-occupancy oxygen atoms. The complexes were grown from acidic solution. One additional proton serves as the counterion to the perchlorate anion from the Pu stock solution. This proton was not explicitly located in the Fourier map, but its position was deduced from particular bond lengths and angles. The proton is disordered over two sites: as an $H_5O_2^+$ ion (O38 and O32, 65% occupancy) located 2.72 Å from the major component of the perchlorate anion, and as an H_3O^+ anion (O37, 35% occupancy) located 3.38 Å from the minor component of the perchlorate anion. The O38–O32 distance is 2.51 Å, a reasonable distance for the $H_5O_2^+$ ion assignment,[15] with O38 hydrogen-bonded to the perchlorate oxygen O44A, and O32 hydrogen-bonded to amide carbonyl oxygen atoms O9 (2.85 Å) and O12 (2.90 Å). The hydronium ion O37 is associated with the perchlorate oxygen O41B, and loosely hydrogen-bonded to the amide carbonyl oxygen atoms O9 (2.98 Å) and O24 (2.91 Å).

Protonation of the metal complex itself can be ruled out for several reasons. First, there are no unusually long Pu–O bond lengths in either Pu coordination sphere to indicate a protonated HOPO oxygen atom. All of the Pu–O bond lengths in each molecule are similar. Second, the [Pu{5-LIO(Me-3,2-HOPO)}$_2$] should be a much weaker base than water. If it is assumed that the formation constants for Pu complexes are the same as those for Ce complexes in which the Ce is in the same oxidation state and if the change of acidity of the Ce^{III}/Ce^{IV} complexes parallels that of the aquo ions, then the formation constant found for the protonated Ce^{III} complex (pK_a ~3) leads to a rough estimate of the pK_a of the protonated Pu^{IV} HOPO complex that is somewhere between −2 and −3, much more acidic than the conditions used here. See reference [11] for more information.

On first inspection, it would appear that the two independent Pu complexes are mirror images of each other. The coordination geometries of the two complexes are of opposite chirality; however, analysis confirms the space group assignment of *Pna*2$_1$ rather than the centric *Pnma* (after transforming the cell). Figure 5 illustrates the difference of the two molecules; a mirror image of the complex structure about Pu2 generated from the atom coordinates is depicted as a wire frame and overlaid onto the molecular structure of Pu1, shown as a ball and stick figure. Rotated such that one of the 5LIO(Me-3,2-HOPO) ligands on each Pu match as closely as possible, it is clear these are non-superimposable.

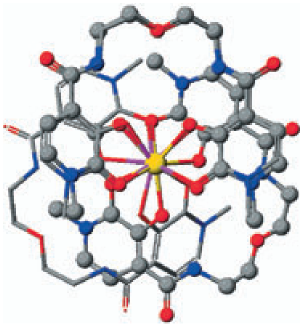


Figure 5. The mirror image of the complex structure about Pu2 (wire frame) is overlaid on that of Pu1 (ball and stick) and rotated such that one of the 5LIO(Me-3,2-HOPO) ligands on each Pu match as close as possible (C: gray; O: red; N: blue; Pu1: yellow; Pu2 is purple to better illustrate the difference in angles). The hydrogen atoms have been omitted for clarity.

While each Pu has the two 5LIO(Me-3,2-HOPO) ligands displaced approximately 135° from each other, the ligands about Pu1 are closer to planar, whereas in the Pu2 molecule one HOPO unit is slightly twisted (Figure 6). There is a slight difference (less than 5°) in the angle by which the HOPO subunits on Pu2 are bent toward the plane generated by the Pu and the linker. This accounts for the slightly longer average plutonium–oxygen bond lengths for the phenolic and amide oxygen atoms in the Pu2 molecule, and is best shown in the side view of the two molecules (Figure 2). This difference is remarkable, especially considering that the ligand displacement seen here is comparable to the 133° displacement seen in the Ce^{IV} structure of the crystals grown from CH$_3$OH, while in the aqueous Ce^{IV} complex a 35° displacement was observed (Figure 7). This is an interesting example of the results of solvent hydrogen bonding and crystal packing modes, and it would be interesting to probe what causes this difference.

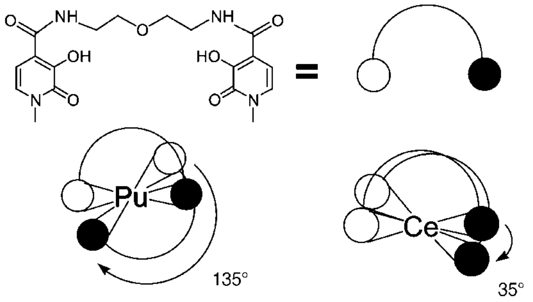


Figure 6. Representation of the ligand offset. The half circle representing the ligand must be rotated 135° to match the ligand system seen in the plutonium structure, whereas it is only rotated by 35° in the cerium structure from the aqueous system.

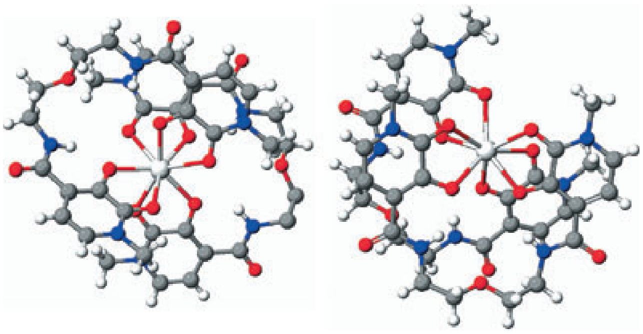


Figure 7. Molecular structures of the Ce^{IV} complexes: [Ce^{IV}{(5-LIO-Me-3,2-HOPO)}$_2$]·4H$_2$O (left) and [Ce^{IV}{(5-LIO-Me-3,2-HOPO)}$_2$]·2CH$_3$OH (right). These figures were generated by using CAChe (C: gray; O: red; N: blue; Ce: white; H: smaller and white).[12]

Few structures of plutonium complexes have been characterized, making comparisons limited. One related Pu^{IV} complex has been described, that of the siderophore desferrioxamine E (DFO-E) with Pu^{IV}.[6] Like the HOPO ligands, the DFO-E also features hydroxamic acid chelating units coordinated to the metal center. In this system, the Pu metal ion is nine-coordinate, coordinated by the macrocycle and three water molecules, and forms a distorted tricapped-trigonal prism geometry. Again, there are two types of Pu–O distances, Pu–O(carbonyl) and Pu–O(amine), with the average Pu–O(carbonyl) bond length being 0.06 Å longer. This is a smaller difference than that found in the 5LIO(Me-3,2,-HOPO) complexes of Pu^{IV} and Ce^{IV}, as well as other hydroxylmate M^{IV} complexes, including the Th^{IV}-Pr(Me-3,2-HOPO) (**3**) reported previously,[16,17] and is perhaps in part due to the increased flexibility of the chelating hydroxamate unit in the DFO-E structure.

The ideal coordination systems for eight-coordinate systems can be categorized by three high-symmetry polyhedra: the trigonal dodecahedron (D_{2d}), bicapped trigonal prism (C_{2v}), and square antiprism (D_{4d}).[18,19] Deciding which of these geometries is closest to an experimental structure is not straightforward. We have described a shape measure, S, to compare the geometries of eight-coordinate systems and group them according to the high symmetry polyhedra they most closely resemble. In this model, S is defined according Equation (1), where m is the number of edges of the coordination polyhedron, δ_i is the observed dihedral angle along the ith edge (the angle between normals of adjacent faces), θ_i is the same angle of the corresponding ideal polytopal shape and min is the minimum of all possible values. Thus, this minimization compares all possible orientations of the observed structure (δ) relative to the reference polyhedron (θ). The value $S(\delta,\theta)$ is a measure (a metric in the strict mathematical sense) of structural resemblance to the idealized shape. This allows comparison of all possible orientations of the observed structure relative to the reference polyhedron and allows the direct comparison of dissimilar complexes formed by various metal ions and ligands.[11]

$$S = \min\left[\sqrt{\frac{1}{m}\sum_{i=1}^{m}(\delta_i-\theta_i)^2}\right] \tag{1}$$

The Ce^{IV} complexes were both assigned to be of square antiprism geometries. The methanolic complex was found to be ($S(D_{2d})=14.33°$) for the trigonal dodecahedron, lower than that of the bicapped trigonal prism ($S(C_{2v})=14.87°$) and the square antiprism ($S(D_{4d})=17.75°$). The lower shape measure for the trigonal dodecahedron clearly shows that the coordination polyhedron is closest to the idealized trigonal dodecahedron, while the complex from the aqueous system is more like the square antiprism. In contrast, both of the Pu molecules in the [Pu^{IV}{5LIO(Me-3,2-HOPO)] complex show that this system is more closely defined as the bicapped trigonal prism, C_{2v} (Table 3). The difference between the shape measure for each system is not as dramatic as that of the [Ce^{IV}{5LIO(Me-3,2-HOPO)}$_2$]·4 H_2O complex, indicating the distortion from any one particular idealized shape. The coordination geometries about the two individual plutonium metal centers are depicted in Figure 8.

Table 3. The shape measure (S) for the given geometry for D_{4d}, C_{3v}, and D_{2d} symmetry is calculated. The Kepert ligand repulsion model with $n=8$ is taken as the ideal geometry here.[20]

	D_{4d}	C_{2v}	D_{2d}
[Pu{5LIO(Me-3,2-HOPO)}$_2$] for Pu1	15.43	13.48	16.10
[Pu{5LIO(Me-3,2-HOPO)}$_2$] for Pu2	15.31	13.21	14.99
[Ce{5LIO(Me-3,2-HOPO)}$_2$]·2 CH_3OH	17.75	14.87	14.34
[Ce{5LIO(Me-3,2-HOPO)}$_2$]·4 H_2O	12.54	18.56	20.68

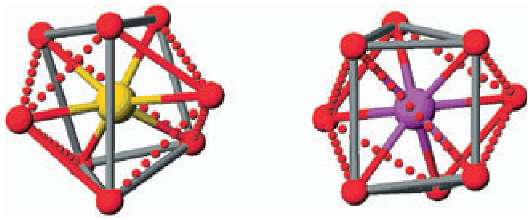


Figure 8. Coordination polyhedra for the two unique plutonium molecules in the unit cell. The solid bonds connect the oxygen atoms of each of the bidentate chelating subunits of the somewhat distorted bicapped trigonal prism (C_{2v}) geometry.

Conclusion

The [Pu^{IV}{5LIO(Me-3,2-HOPO)}$_2$] complex represents the first Pu^{IV} hydroxypyridonate complex to be structurally characterized. Owing to both practical and radiation handling concerns, the structure determination was carried out using a synchrotron radiation source. The differences between the two unique molecules found in the unit cell, and the difference between this structure and that of the related Ce^{IV} complex prepared from water, lends interest to further probing the influence of solvent systems, pH, and hydrogen bonding on crystal packing. The [Pu^{IV}{5LIO(Me-3,2-HOPO)}$_2$] complex is the first in a series to be characterized with the intent of generating a library of such systems on which to base the modeling and design of future systems, and provide a benchmark for additional structural studies such as EXAFS (extended X-ray absorption fine structure).

Experimental Section

General: Procedures with ^{242}Pu were conducted in a glove box under negative pressure designed for the safe handling of radionuclides. Liquid scintillation counting was performed with a Wallac Guardian 1414 LSC, and the scintillation cocktail was Eco-Lume (ICN). Bulk electrolysis using a Ag/AgCl reference electrode was conducted in a 100-mL glass beaker fitted with a stir bar, a platinum mesh working electrode, an Ag/AgCl reference electrode, and a platinum counter electrode. An IBM Voltammic analyzer was used to adjust the potential. The 5-LIO(Me-3,2-HOPO) ligand **1** (5-LIO(Me-3,2-HOPO) = 3-hydroxy-1-methyl-2-oxo-1,2-dihydro-pyridine-4-carboxylic acid (2-{2-[(3-hydroxy-1-methyl-2-oxo-1,2-dihydropyridine)amino]ethoxy}ethyl)amide) was synthesized by previously published methods[11] using reagents and solvents from the Aldrich Chemical Company and used as purchased. Solvents were dried over activated alumina and stored over 4 Å molecular sieves. Water was distilled and further purified by a Millipore cartridge system (resisitivity $18\times10^6\ \Omega$).

Pu stock solution preparation: The ^{242}Pu was received from Oak Ridge National Laboratory as PuO_2 (lot Pu-242–327 A, 99.93 wt % of metal ^{242}Pu). The solid was dissolved in concentrated nitric acid with heating. The ^{242}Pu stock solution was loaded onto a 400 mesh Dowex anion exchange resin column and washed with 7.5 M HNO_3 to remove any daughter products; the ^{242}Pu was isolated as the nitrate. The plutonium was then eluted with 0.4 M HCl with a trace of HF to strip the Pu^{IV} from the column. The plutonium eluent was then transferred to a round-bottomed boiling flask fitted with a condensing arm and KOH traps to collect acid vapors, and boiled to dryness. The remaining salt was dissolved in concentrated HNO_3 and boiled for three hours to digest any organic material present in the sample. The solution was concentrated by evaporation. Concentrated perchloric acid was added to the solution, and it was boiled for three hours. Fresh perchloric acid was continually added to maintain the solution volume until the nitrate was removed. The resulting characteristically yellow Pu^{VI} solution was adjusted to Pu^{III} by electrochemical reduction. The Pu^{IV} stock solution can be prepared as needed by oxidation of the Pu^{III} stock. The final concentration of the plutonium stock solution was determined by alpha liquid scintillation counting.

Pu complex preparation: An aliquot of the Pu^{IV} stock solution was diluted with deionized water and the concentration of Pu^{IV} was found to be $0.01\,mol\,L^{-1}$ by scintillation. The resulting solution was 1.1 M $HClO_4$. 5LIO(Me3,2-HOPO) (2.1 mg, 4.9×10^{-3} mmol) was dissolved in deionized H_2O (2 mL) that had been warmed to 40 °C. To this, Pu^{IV} stock solution (230 µL, 2.3×10^{-3} mmol, 1:2.1, M:L) was added. The solution turned an amber color with the addition of the metal. The pH was found to be close to 5 using pH paper. This solution was set aside to allow time for evaporation and crystallization of the complex. After two weeks, the remaining solution appears yellow and crystals were obtained as dark purple plates. A couple of the larger crystals were found to be suitable for X-ray diffraction. The remaining solution has a pH close to 2 by pH paper. After four weeks, the sample was sealed with Parafilm to prevent any additional solvent loss. The complex is quite robust, signs of decomposition, believed to be the result of solvent loss, are seen only after six months.

Crystal preparation and mounting: The crystals, while not air- or water-sensitive, require great care and special handling for mounting and transport to the diffractometer at the ALS. Suitable crystals were identified for analysis and mounted inside 0.3-mm quartz capillaries in Paratone-N oil, while still inside the glove box. The capillaries were then coated with a protective resin prior to being cut to fit into the goniometer such that the crystals would be properly illuminated in the X-ray beam. These were then sealed with epoxy resin and marked to prevent any damage or loss. The capillaries were secured in brass pins for mounting on the goniometer with wax and epoxy resin. Crystals were transported from the lab in a sealed container already mounted on the goniometer heads, thus minimizing the amount of alignment required once at the diffractometer. A detailed description of the crystal mounting procedure and handling technique is available in reference [20]. Additional measures were taken to protect the data collection equipment at the beamline from contamination. These include the protective coating and markings on the capillary, covering the optical table on which the goniometer is mounted, and the design and construction of a "catcher" that fits onto the goniometer to prevent losing the capillary, should an event occur in which the capillary was dislodged from the goniometer.

Structure determination and refinement: Special procedures were developed for X-ray diffraction crystal structure determination of radioactive samples using synchrotron radiation. Crystallographic data were collected by using a Bruker Platinum 200 detector at the Small-Molecule Crystallographic Beamline 11.3.1 at the ALS. The goniometer is mounted vertically and has a chi angle of 54.7°. Intensity data were collected at 298 K (room temperature) in less than one hour using Bruker Apex II software.[21] A series of 1-s data frames measured at 0.2° increments of ω were collected to calculate a unit cell and to measure a hemisphere of intensity data. Peak integrations, cell refinement, and data reduction were performed by using the Bruker SAINT software package.[22] Data were corrected for absorption using SADABS.[23] Dispersion factors (f and f') at 16 keV for C, N, O, and Cl were input using values from CROMER for Windows. Dispersion factors for Pu were interpolated and imported for use in SHELXS using literature data.[24] The structure was solved with direct methods using SHELXS, and the space group assignment was confirmed by using a Patterson map. Least-squares refinement was performed by using SHELXL.[25]

All non-hydrogen atoms except perchlorate atoms and solvent oxygen atoms were refined anisotropically. Hydrogen atoms were included in calculated idealized positions for non-solvent atoms. Methyl hydrogen atoms were refined with isotropic thermal parameters 1.5 times that of the carbon to which they are bonded. All other hydrogen atoms were refined with isotropic thermal parameters 1.2 times that of the atom to which they are bonded. The disordered perchlorate anion was modeled as two fragments whose occupancies were refined but summed to one. The geometry of each fragment was constrained as a rigid body to an idealized tetrahedron with Cl–O bond lengths of 1.407 Å. The two Cl thermal parameters were refined isotropically and set equal to one another, as were the eight perchlorate oxygen thermal parameters. The occupancies for the $H_5O_2{}^+$ fragment (O32 and O38) and the H_3O^+ ion (O37) were constrained to equal the site occupancy factors for the major and minor components of the perchlorate ion, respectively.

Crystal data: The crystallographic parameters for [Pu{5LIO(Me-3,2-HOPO)}$_2$] ($C_{72}H_{80}ClN_{16}O_{38.65}Pu_2$, formula weight $=2321.48\,g\,mol^{-1}$, dark purple plates ($0.070\times0.050\times0.025$ mm) grown from an aqueous solution) are: space group $Pna2_1$, $a=26.084(5)$, $b=23.439(4)$, $c=15.564(3)$ Å, $V=9516(3)$ Å^3, $Z=4$, $\rho_{calcd}=1.620\,g\,cm^{-3}$. The data were collected at 298 K using a Bruker Platinum 200 detector with 16 keV synchrotron radiation from the Small-Molecule Crystallographic Beamline 11.3.1 at the Advanced Light Source (ALS). A total of 63115 (16280 independent) reflections were collected. The structure was solved by using direct methods, and the space group was confirmed by Patterson methods. The structure was found to be a simple inversion twin, with twin law [−1000−1000−1]. The twin components were refined to a 62:38 population. Least-squares refinement of F^2 against all reflections was carried out to convergence with $R[I>2\sigma(I)]=0.0638$ for 11214 reflections and $wR2=0.1981$ for 16280 reflections and 1123 parameters, with a goodness of fit of 1.039.

CCDC-249885 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We thank the following for their assistance with this project: Dr. Allen Oliver and Dr. Fred Hollander with X-ray crystallography, Brian Fairchild ALS/LBNL EH&S, Sirine Fakra ALS, Lindsy Farina, Dr. Wayne Lukens, and Mario Cepeda and John Schaffer of Design Works Plus (Engineering Division, LBNL) for CAD and fabrication of the safety catcher. This research and the ALS are supported by the Director, Office of Basic Energy Sciences, Division of Materials Sciences and Division of Chemical Sciences, Geosciences, and Biosciences of the U.S. Department of Energy at Lawrence Berkeley National Laboratory under Contract No. DE-AC03–76SF00098. A portion of this research was performed as part of the Office of Civilian Radioactive Waste Management Fellowship Program administered by Oak Ridge Institute for Science and Education under a contract with the U.S. Department of Energy and the Oak Ridge Associated Universities (R.E.W.).

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Received: November 23, 2004