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Synthesis and Molecular Structure of a Plutonium(IV) Coordination Complex: $[Pu(NO_3)_2\{2,6\text{-}[(C_6H_5)_2P(O)CH_2]_2C_5H_3NO\}_2](NO_3)_2 \cdot 1.5H_2O \cdot 0.5MeOH$

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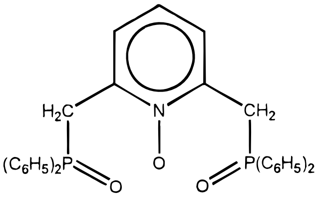
The trifunctional ligand 2,6-$[(C_6H_5)_2P(O)CH_2]_2$ C_5H_3NO (**1**), in a mixed EtOH/MeOH solvent system, when combined with an aqueous nitric acid solution of Pu(IV), produces a 2:1 coordination complex, $[Pu(\mathbf{1})_2(NO_3)_2](NO_3)_2$. A single crystal of $[Pu(NO_3)_2\{2,6\text{-}[(C_6H_5)_2P(O)CH_2]_2C_5H_3NO\}_2](NO_3)_2 \cdot 1.5H_2O \cdot 0.5MeOH$ was characterized by X-ray diffraction analysis. The crystal is monoclinic, space group $P2_1/n$, with $a = 19.1011(9)$ Å, $b = 18.2873(9)$ Å, $c = 21.507(1)$ Å, $\alpha = \gamma = 90°$, $\beta = 108.64(1)°$, and $Z = 4$. Two neutral ligands (**1**) are bonded to the Pu(IV) ion in a tridentate fashion. Two nitrate ions also occupy inner sphere coordination positions, while two additional NO_3^- ions reside in the outer sphere. Comparison of the solution optical absorbance and solid diffuse reflectance spectra shows the same Pu(IV) chromophore exists in both solid and solution states.

Introduction

Recently, the trifunctional ligand 2,6-$[(C_6H_5)_2P(O)CH_2]_2C_5H_3NO$ (**1**) has been observed to form strong coordination complexes with oxophilic trivalent lanthanide cations, and it generally binds to these metals in a tridentate fashion through the pyridine *N*-oxide and phosphoryl oxygen donor sites.[1−3] The ligand also acts as a powerful liquid−liquid extractant of trivalent lanthanide ions and Am(III)[3−5] from concentrated HNO_3 and HCl solutions. Since several tetravalent cations are found in some nuclear material solutions containing trivalent ions, the coordination and extraction chemistry of **1** with these ions is of interest. Indeed, we have previously reported that **1** forms a 2:1 complex with Th(IV), and preliminary studies indicate that Th(IV) is extracted from HNO_3 solutions by $CHCl_3$ solutions of **1**. These results have encouraged development of modified ligand designs[6] as well as additional studies of the coordination chemistry of **1**. We report here the formation and structure determination of the 2:1 complex of **1** with Pu(IV), an actinide ion for which very few coordination complexes have been isolated and structurally characterized by single-crystal X-ray diffraction methods.



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Experimental Section

The ligand 2,6-bis[(diphenylphosphino)methyl]pyridine *N*,*P*,*P′*-trioxide was prepared according to the published procedure.[2] Standard radiochemical procedures were used for the synthesis of the complex. All the manipulations were performed in either HEPA-filtered fume hoods or negative pressure gloveboxes. Methanol and ethanol were obtained from J.T. Baker and were used without further purification. A plutonium-239 stock solution was prepared and purified as described in the literature.[7,8] The solution purification used anion exchange chromatography (Lewatite MP-500) that binds Pu(IV) as $(Pu(NO_3)_6^{2-})$. The Pu(IV) was recovered by eluting with 0.5 M HNO_3. The stock solution was assayed by UV/vis spectroscopy to verify the oxidation state purity and to determine the plutonium concentration. The Pu(IV) oxidation state was confirmed and the metal content assayed by using a characteristic absorbance band at 470 nm ($\epsilon = 58$ M^{-1} cm^{-1}).[8−11] UV/vis/near-IR absorbance spectra were obtained on a Cary 500 (Varian) spectrophotometer, and diffuse reflectance spectra were measured with a Lambda-19 (Perkin-Elmer) spectrophotometer.

Preparation of $[Pu(1)_2(NO_3)_2^{2+}][(NO_3)_2^{2-}] \cdot 1.5H_2O \cdot 0.5MeOH$. The complex was prepared by adding a 100 μL aliquot of a 0.08 M

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Table 1. Summary of Crystallographic Data

empirical formula	$C_{62.5}H_{56}N_6O_{20}P_4Pu$	cell vol (Å^3)	7118.6(6)
fw	1572.73	Z	4
space group	$P2(1)/n$	calcd density (g cm^{-3})	1.467
a (Å)	19.1011(9)	T (K)	293
b (Å)	18.2873(9)	λ (Å)	0.710 73
c (Å)	21.507(1)	μ (mm^{-1})	1.105
α (deg)	90	R1^a, ($I > 2\sigma(I)$)	0.0368
β (deg)	108.64(1)	wR2^b	0.0978
γ (deg)	90		

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)/3$.

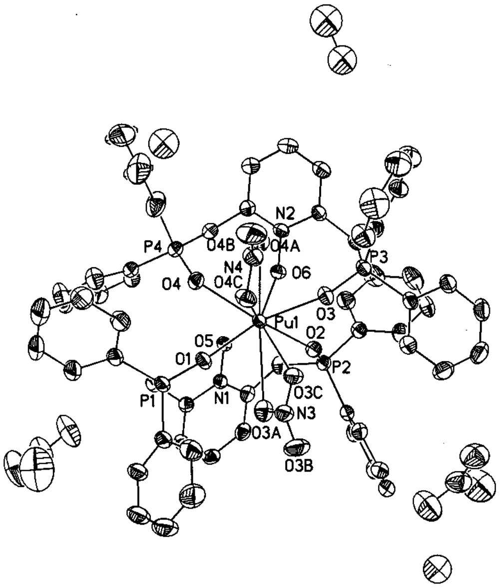

Figure 1. Thermal ellipsoid (30%) plot of $[Pu(\mathbf{1})_2(NO_3)_2{}^{2+}][(NO_3)_2{}^{2-}]\bullet 1.5H_2O\bullet 0.5MeOH$.

solution of $Pu(NO_3)_6{}^{2-}$ in 0.5 M HNO_3 to **1** (0.0042 g, 8.0 μmol) dissolved in a 1:5 mixture of MeOH/EtOH. Upon addition, the solution turned orange-brown. The vial containing the mixture was closed, and orange-brown X-ray-quality crystals formed after a few days. Crystal samples were both ground to a fine powder and dissolved in MeOH to obtain the diffuse reflectance and optical absorbance spectra, respectively.

Crystallographic Analysis. Suitable crystals were selected from samples prepared as described above and coated with a thin protective film of 5 min epoxy. The coated crystals were then sealed in glass capillaries that were also coated on the outside with acrylic to provide structural stability to the capillaries and multiple containment of the radioactive material. The crystals were screened for maximum scattered intensity, and the best crystal was utilized for data collection. Crystallographic data for the complex are presented in Table 1. Diffraction data were collected at ambient temperature on a Bruker P4/PC diffractometer equipped with a CCD area detector. Data were collected using both ϕ- and ω-scan methods; a full hemisphere of data were collected. The program SADABS[12] was used to correct for absorption and decay. The structure was solved by Patterson and difference Fourier methods with the program SHELXS-97.[13] All other non-hydrogen atoms were found by least-squares refinement and subsequent difference Fourier analysis using SHELXL-97.[14] All atoms except for the solvent molecules were refined anisotropically to convergence. Refinement on F^2, for 842 parameters and 9880 unique reflections, gave R1 = 0.0368, wR2 = 0.0978. An ORTEP plot (30% thermal ellipsoids) of the molecule is shown in Figure 1.

Results and Discussion

As noted in the Introduction, the recently designed and synthesized ligand 2,6-bis[(diphenylphosphino)methyl]pyridine *N*,*P*,*P′*-trioxide (NOPOPO),[1,2] **1**, has proven to be an excellent extractant for trivalent lanthanide and actinide ions in nitrate or chloride media. It displays partition coefficients significantly higher than those reported for the classic bifunctional extractants dihexyl-*N*,*N*-diethylcarbamoylmethylphosphonate (DHDECMP), $(HxO)_2P(O)CH_2C(O)NEt_2$,[15,16] and octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (CMPO), $(Oct)(Ph)P(O)CH_2C(O)N(^iBu)_2$.[17] Our earlier structural studies of isolated complexes formed by **1** and lanthanide nitrates and chlorides[1,2,18] show several interesting features. For all cases, the ligand adopts a tridentate coordination mode. In 1:1 ligand/metal complexes, three nitrate ions remain bonded to the Ln(III) ion in a bidentate manner,[1] and in 2:1 complexes, only one bidentate nitrate ion is present in the inner coordination sphere.[1] The remaining two nitrates are expelled to the outer sphere. In the same work, we observed that the interaction of **1** with $Th(NO_3)_4$ gives a 2:1 complex, $[Th(\mathbf{1})_2(NO_3)_2](NO_3)_2$, in which two molecules of **1** bond to the Th(IV) in a tridentate fashion, and two nitrates remain in the inner coordination sphere.[1] The remaining two nitrate ions appear in the outer sphere. Recently, we have found that $EuCl_3$ in water combines with **1** in a 2:1 L/M ratio, giving a complex containing two tridentate ligands **1** and two water molecules in the inner sphere. The more weakly binding Cl^- ions all appear in the outer sphere along with nine water molecules.[18]

The interesting coordination behavior of **1** toward lanthanide(III) and thorium(IV) nitrates encouraged us to examine the coordination chemistry of **1** with Pu(IV) since the molecular structures of this very important actinide ion have been little studied. The 2:1 ligand/metal complex was prepared by combining a 1 M HNO_3 solution of $Pu(NO_3)_6{}^{2-}$ and an alcohol mixture of the ligand. This combination allows for the crystallization of the product as it forms. The UV/vis/near-IR spectra of the complex (Figure 2) were obtained from two samples. The dashed line represents the diffuse reflectance of ground crystals, and the solid line corresponds to the absorbance of a methanol solution of the isolated crystals. The two spectra are similar except for band splitting and resolution differences in the features at 1200−1050, 850, 680−620, and 570−510 nm. One may expect peak splitting and greater resolution in solid-state spectra where there are no interactions with solvent and less rotation and vibration. The spectra are similar to those of other Pu(IV) complexes with oxygen donor ligands;[7,9−11] however, it is expected that additional studies of related complexes may begin to reveal spectral features, diagnostic of structural details.

Single crystals of the coordination complex, deposited from the reaction solution, were characterized by X-ray diffraction

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Table 2. Selected Bond Distances (Å)

Pu(1)−O(1)	2.310(4)	Pu(1)−O(4A)	2.710(5)	N(2)−O(6)	1.343(6)
Pu(1)−O(6)	2.338(4)	Pu(1)−O(3A)	2.824(5)	N(3)−O(3B)	1.212(7)
Pu(1)−O(3)	2.339(4)	P(1)−O(1)	1.502(4)	N(3)−O(3A)	1.233(7)
Pu(1)−O(5)	2.346(4)	P(2)−O(2)	1.499(4)	N(3)−O(3C)	1.308(7)
Pu(1)−O(2)	2.357(4)	P(3)−O(3)	1.504(4)	N(4)−O(4B)	1.202(7)
Pu(1)−O(4)	2.382(4)	P(4)−O(4)	1.490(4)	N(4)−O(4A)	1.256(7)
Pu(1)−O(4C)	2.425(4)	N(1)−O(5)	1.334(6)	N(4)−O(4C)	1.270(7)
Pu(1)−O(3C)	2.429(4)				

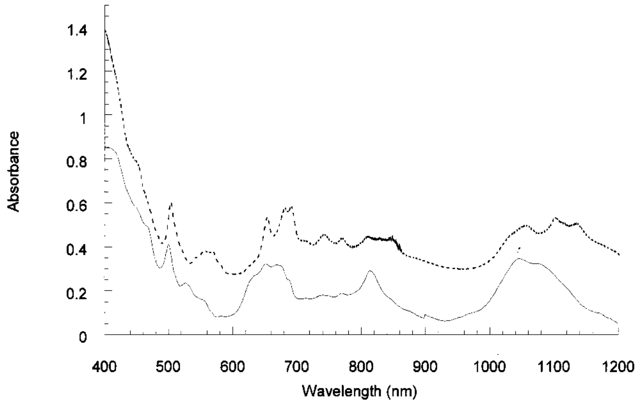

Figure 2. UV/vis/near-IR spectrum for $[Pu(\mathbf{1})_2(NO_3)_2][(NO_3)_2]$: diffuse reflectance of ground crystals (dashed line); isolated crystals dissolved in MeOH (solid line).

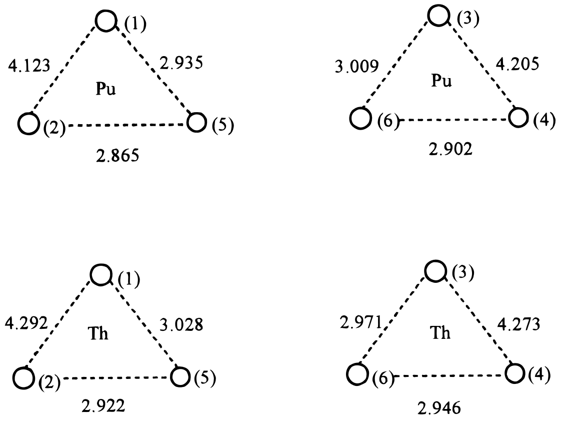

Figure 3. Coordination footprints for **1** on Pu(IV) and Th(IV).

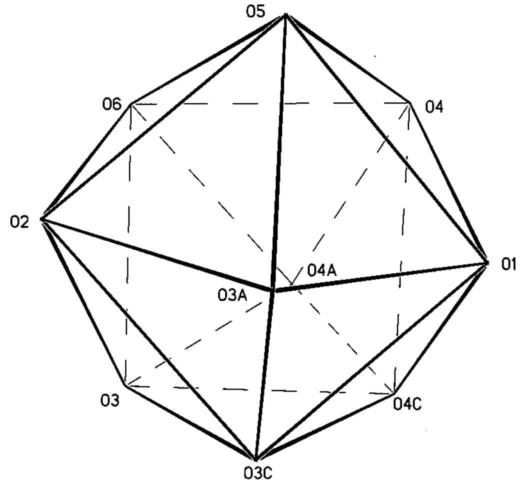

Figure 4. Coordination sphere for $[Pu(\mathbf{1})_2(NO_3)_2{}^{2+}][(NO_3)_2{}^{2-}]\bullet 1.5H_2O\bullet 0.5MeOH$ with phenyl rings and outer-sphere nitrates omitted for clarity.

analysis. The molecular structure contains two molecules of **1** bonded to the central Pu(IV) ion in a tridentate mode. In addition, there are two nitrate ions coordinated in an asymmetric bidentate fashion to the Pu(IV) ion. The Pu−O(P) bond lengths range from 2.310(4) to 2.382(4) Å (av 2.347 Å) and are all shorter than the average value in $[Th(\mathbf{1})_2(NO_3)_2](NO_3)_2$, 2.402(1) Å.[1] The Pu−O(N) bond lengths, 2.338(4) and 2.346(4) Å, are also shorter than the comparable distances in the Th(IV) complex, 2.391(1) and 2.400(1) Å. These shorter Pu−O bond lengths are consistent with the smaller Pu(IV) (CN = 8, r = 0.96 Å) ionic radius compared to that of Th(IV) (CN = 8, r = 1.06 Å).[19] The ligand "footprints" of **1** on the Pu(IV) ion, compared to the "footprints" on Th(IV), are smaller on five of the six nonbonded O···O edges as shown in Figure 3. This is expected for the smaller, more polarizing Pu(IV) ion. As observed in the Th(IV) complex, the two inner-sphere nitrates bind to the Pu(IV) with an asymmetric bidentate bite: Pu−O(3A) 2.824(5) Å, Pu−O(3C) 2.429(4) Å, Pu−O(4A) 2.710(5) Å, and Pu−O(4C) 2.425(4) Å. Space-filling diagrams suggest that there is adequate room for each O(A) atom to form a shorter interaction with the plutonium; however, because of the four-atom metal−nitrate chelate rings and the near 120° angle between the nitrate oxygen atoms, shorter, more symmetrical interactions would require a considerable rearrangement of the inner coordination sphere. The asymmetric nitrate ion bite found in this complex contrasts with the more symmetrically bonded nitrate ions in $[NH_4]_2[Pu(NO_3)_6]$.[20] In the latter case the average Pu−O (nitrate) bond length is 2.487 Å. Furthermore, because of the asymmetric interaction of the nitrate ions with the Pu(IV) center, there are three different N−O distances, with the longest being O(C) to N, the second longest O(A) to N, and the shortest O(B) to N, which corresponds to the shortest M−O distance, second shortest, and longest, respectively. The average values of the P═O and N−O bond lengths in the Pu(IV) complex are 1.498 and 1.32 Å, respectively. These values are little changed from the values found for the free ligand: P═O 1.480(3) Å and N−O 1.315(6) Å.[2]

Three idealized polyhedra are predicted to have similar low energies for the CN = 10 condition: bicapped square antiprism and sphenocorona and tetracapped trigonal prism.[21] Analysis of the nonbonded O···O contact distances for the 10 inner-sphere oxygen atoms in $[Pu(\mathbf{1})_2(NO_3)_2{}^{2+}]$ suggests that they best approximate a distorted bicapped square antiprism as shown in Figure 4. The two capping positions are occupied by O(3A) and O(4A), and the nitrate ion bond distance constraints "pull" these atom positions off the ideal square antiprism axis. It is noteworthy that the distortion results in the two nitrates occupying positions on one side of the polyhedron while the two ligands **1** cover the majority of the volume of the polyhedron.

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The X-ray diffraction analysis described here represents the first single-crystal structure determination for a plutonium complex with an organic extraction agent. The structure indicates the ready tendency for **1** to reorganize, from its free ligand structure, in which the P═O bond vectors point away from the N─O bond vector,[2] into the tridentate chelate condition. This is possible because of the rotational freedom in the pendant (ring)─CH_2─P(O)Ph_2 arms. Placement of the two bulky ligand units of **1** on the central metal creates an organic "mushroom cap" that is organophilic and is largely responsible for the organic solvent solubility of the Th(IV) and Pu(IV) complexes. This in turn permits phase transfer of the metal from an acidic aqueous phase to an organic phase in a liquid─liquid extraction. In the future we expect to study the extraction phase transfer process as well as back-extraction behavior with the intent to develop an advanced Pu(IV) separation scheme.

Electronic spectral data are routinely used to identify oxidation states, coordination numbers, and geometries in d-block metal complexes. These data have also been used for identifying oxidation states in actinide ion complexes; however, less systematic information has been derived that is diagnostic of coordination structure. The solid-state and solution spectroscopic data reported here are important as we continue to catalog and define spectroscopic features that are indicative of coordination numbers and geometries in plutonium complexes.

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Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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