Inorganic Chemistry

Communication

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$[N(n\text{-}Bu)_4]_2[Pu(NO_3)_6]$ and $[N(n\text{-}Bu)_4]_2[PuCl_6]$: Starting Materials To Facilitate Nonaqueous Plutonium(IV) Chemistry

Sean D. Reilly,[†] Brian L. Scott,[‡] and Andrew J. Gaunt*[,†]

[†]Chemistry Division and [‡]Materials Physics and Applications Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States

Supporting Information

ABSTRACT: The reaction of plutonium(IV) in aqueous nitric acid with tetra-*n*-butylammonium nitrate leads to the immediate precipitation of $[N(n\text{-}Bu)_4]_2[Pu(NO_3)_6]$ (**1**) in high yield. The analogous reaction in HCl with tetra-*n*-butylammonium chloride gives $[N(n\text{-}Bu)_4]_2[PuCl_6]$ (**2**). Both **1** and **2** are soluble in a range of organic solvents and have been characterized by single-crystal X-ray diffraction, IR spectroscopy, and solid- and solution-phase vis−near-IR spectroscopy. **1** and **2** provide facile synthetic entry routes to study plutonium(IV) ligand complexation reactions in organic solvent media under both air/moisture-stable and -sensitive conditions.

The study of plutonium−ligand coordination chemistry under nonaqueous conditions is hindered by the fact that, to date, very few plutonium(IV) starting materials exist that are soluble in organic solvents.[1] An obvious prerequisite of elucidating the bonding properties of plutonium is that molecules need to be synthesized and isolated in pure form. On a practical and logistical level, this task is much more difficult for the transuranic elements than it is for thorium, uranium, and nonradioactive metals for several reasons that are not often explained in the literature to the nonspecialist, and we elaborate in the following paragraph.

Aqueous acidic plutonium(IV) is sometimes used and spiked into an organic solvent containing the ligand to be studied.[2] However, this approach is obviously not suitable when the target plutonium−ligand complex is air- and/or moisture-sensitive. Even for air/moisture-stable systems, the large excess of acid often present relative to the plutonium(IV) concentration can be a complicating factor. The Pu^{4+} cation is highly prone to hydrolysis and the formation of insoluble hydroxide precipitates; thus, aqueous plutonium(IV) stock solutions often contain millimolar plutonium(IV) in (multi)molar nitric or hydrochloric acid. However, NO_3^- and Cl^- anions form complexes with plutonium(IV) of the type $[PuX_n]^{(4-n)+}$ ($X = NO_3^-, Cl^-$; $n = 1-6$), leading to competition with the ligand to be studied. Attempts at growing plutonium crystals by evaporation may also lead to the precipitation of undesired excess inorganic salt instead. A further complicating factor is the fact that most basic research efforts that utilize transuranic radionuclides are confined to small milligram scales, which can pose reproducibility issues. Other elements in the periodic table often benefit from a good choice of available precursors, up to gram-scale reactions, and the ability to repeat a reaction many times with “tweaks and modifications” in the reaction conditions. None of these options are readily available for the syntheses, isolation, and characterization of plutonium complexes because of the limited quantities available in most basic research-oriented radiological facilities.

These limitations led us to search for plutonium(IV) synthetic starting materials to fulfill important criteria: (1) be precipitated from aqueous solution [the only readily available source of plutonium(IV) in solution], (2) be purified in high yield, (3) be well characterized, and (4) be redissolved in an organic solvent for subsequent ligand complexation studies. Literature precedent indicated that organic-soluble tetra-*n*-butylammonium (TBA) salts of $[PuX_6]^{2-}$ might be suitable if they could be prepared and precipitated from aqueous solution.[3] While there are previous single-crystal and powder X-ray diffraction studies of a few other salts of $[Pu(NO_3)_6]^{2-}$ and $[PuCl_6]^{2-}$ anions,[2b,3a,4] none fulfills all of the important criteria that allow them to serve as ideal plutonium(IV) synthons.

The alkali-metal salts of $[PuCl_6]^{2-}$ are not soluble in organic solvents. Recently, $[PPh_4]_2[PuCl_6]$ was reported as a high-yield synthesis and structurally characterized as part of a study to prepare salts for X-ray absorption spectroscopy analyses.[4d] Although this compound holds some synthetic utility, it has limited organic solubility (MeCN with heating), which can hamper what should be straightforward reactions. For example, we attempted to prepare $PuCl_2(^{Ar}acnac)_2$ ($^{Ar}acnac$ is a *β*-ketoiminate ligand) by the treatment of 2 equiv of $Na^{Ar}acnac$ with $[PPh_4]_2[PuCl_6]$ in THF solvent. Instead of the expected 1:2 plutonium−ligand product, a 1:4 product was obtained instead because of the local excess of ligand caused by the insolubility of $[PPh_4]_2[PuCl_6]$ prior to ligand complexation.[5] Organic-solvent-soluble Me_4N^+ and Et_4N^+ salts of $[PuCl_6]^{2-}$ have been reported but with no full single-crystal structural determinations and no indication of synthetic yields. A similar picture emerges when one surveys the known simple salts of the $[Pu(NO_3)_6]^{2-}$ anion, for which only $[NH_4]_2[Pu(NO_3)_6]$ has been fully structurally characterized,[4c] again without a reported yield and other supporting characterization.

In this Communication, we present high-yield syntheses, crystal structures, and spectroscopic characterization of $[N(n\text{-}Bu)_4]_2[Pu(NO_3)_6]$ (**1**) and $[N(n\text{-}Bu)_4]_2[PuCl_6]$ (**2**), which fulfill the important criteria described above to serve as useful and reproducible synthetic precursors. The addition of an

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aqueous plutonium(IV)−HNO_3 solution to 2 equiv of TBA nitrate in aqueous 2 M nitric acid led to the immediate precipitation of **1** as a green solid, leaving a colorless solution indicative of near-quantitative plutonium precipitation. Compound **1** is soluble in a range of organic solvents, including MeCN, EtOH, and acetone, but insoluble in Et_2O. **1** also shows slight solubility in water and dilute HNO_3 (<2 M), while it is insoluble in more concentrated nitric acid. This is consistent with previous reports that the quaternary ammonium salts of $[An(NO_3)_6]^{2-}$ are sparingly soluble in 5−9 M HNO_3 but readily soluble in water.[3d] This solubility also presumably contributed to the yield we observed, because in the synthesis we report here, the initial solid precipitate was washed three times with 2 M HNO_3 to remove any unreacted TBA nitrate. Some of product **1** may have been lost during washing, leading to a yield of 80%. Higher yields approaching 100% were obtained when the unwashed solid was directly redissolved in acetonitrile and the solution $[Pu(NO_3)_6]^{2-}$ yield determined by visible−near-IR (vis−NIR) spectrophotometry.

Crystals of **1** suitable for X-ray diffraction were grown by evaporating an acetonitrile solution of compound **1** to near-dryness. Single-crystal structural analysis of **1** confirms a formula of $[N(n\text{-Bu})_4]_2[Pu(NO_3)_6]$ in the crystalline phase (Figure 1), and there are no lattice solvent molecules. The Pu^{IV} center has a coordination number of 12 through binding of the O atoms of six bidentate nitrate anions. The geometry is best described as an irregular icosahedron. The Pu−O distances in **1** range from 2.4736(16) to 2.5017(16) Å, comparing well to those in $[NH_4]_2[Pu(NO_3)_6]$,[4c] and the O−Pu−O nitrate "bite" angles in **1** range from 50.92(5) to 51.66(5)° (Table 1). For comparison to other $[An(NO_3)_6]^{2-}$ anions, the Th−O distances in $[NH_4]_2[Th(NO_3)_6]$ range from 2.545(6) to 2.608(5) Å.[4c] In $[N(n\text{-Bu})_4]_2[U(NO_3)_6]$, the U−O distances range from 2.5013(18) to 2.5313(17) Å,[6] while the Np−O distances in $[C_{10}H_{10}N_2][Np(NO_3)_6]\cdot 2H_2O$ range from 2.455(6) to 2.540(9) Å.[7]

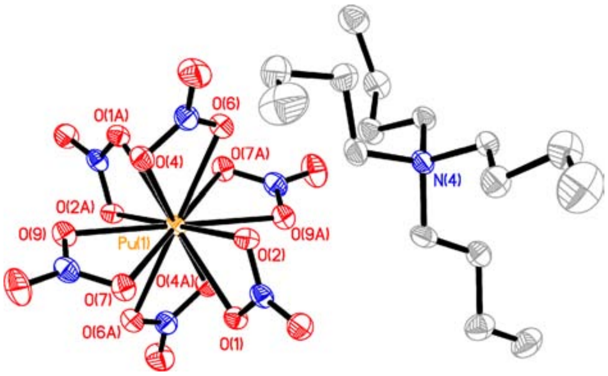

Figure 1. Thermal ellipsoid plot (50% probability level) of the structure of **1**. The H atoms have been omitted, and only one of the two TBA cations is shown for clarity.

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

Pu(1)−O(1)	2.5017(16)	Pu(1)−O(2)	2.5002(16)
Pu(1)−O(4)	2.4891(16)	Pu(1)−O(6)	2.4994(16)
Pu(1)−O(7)	2.4736(16)	Pu(1)−O(9)	2.4738(18)
O(1)−Pu(1)−O(2)	50.92(5)	O(4)−Pu(1)−O(6)	51.16(5)
O(7)−Pu(1)−O(9)	51.66(5)		

The vis−NIR solution spectrum of compound **1** dissolved in acetonitrile is shown in Figure 2. This spectrum closely matches spectra attributed to the $[Pu(NO_3)_6]^{2-}$ anion in 13.2 M HNO_3 and MeCN.[3b] This suggests that the $[Pu(NO_3)_6]^{2-}$ anion does not dissociate to an appreciable extent in MeCN.[8] The solid-state diffuse-reflectance spectrum of pure compound **1** is also shown in Figure 2. It is evident that the solution and solid-state vis−NIR spectra of **1** in Figure 2 have differences. One interpretation is that the solution spectrum is not that of pure $[Pu(NO_3)_6]^{2-}$. This seems unlikely given the evidence above. Alternatively, it is possible that the nitrate 12-coordinate geometries are slightly different in solution versus solid states, resulting in differences in the vis−NIR spectra. Interestingly, a discrepancy was also noted in a study of $[Pu(NOPO)_2(NO_3)_3][Pu(NO_3)_6]_{0.5}$ (NOPO = phosphinomethylpyridine *N*,*P*-dioxide),[2b] for which the solution UV−vis spectrum did not contain absorptions previously observed in solid-state UV−vis spectra of other $[Pu(NO_3)_6]^{2-}$-containing salts (cited as unpublished results, but a few bands were listed and correlate well with those in the solid-state electronic absorption spectrum of **1**).

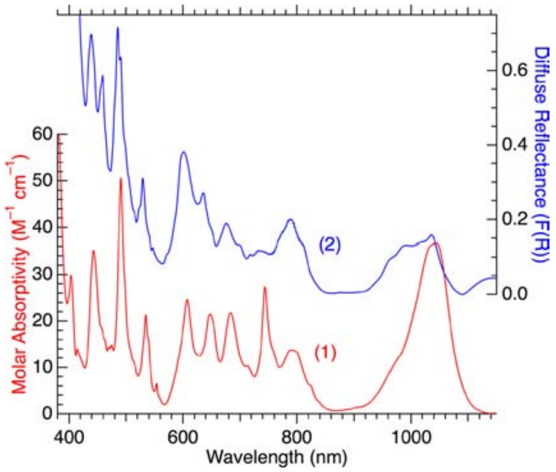

Figure 2. Solution electronic absorption spectrum of compound **1** dissolved in MeCN [red spectrum (1), left axis] and diffuse-reflectance spectrum of solid compound **1** [blue spectrum (2), right axis].

The IR spectrum of solid $[n\text{-Bu}_4N]_2[Pu(NO_3)_6]$ as a Nujol mull and the Raman spectrum of solid $[n\text{-Bu}_4N]_2[Pu(NO_3)_6]$ were also recorded (see the Supporting Information). Compound **1** stored in the solid state appears to partially decompose over the course of several days, as is evidenced by the incomplete dissolution of aged solids in acetonitrile. Acetonitrile solutions of freshly prepared **1** appear stable for at least several weeks because no precipitation or change in the solution vis−NIR spectrum was observed.

Given the high-yield synthesis of **1**, we then turned to the analogous chloride system. No immediate precipitation occurred upon the addition of an aqueous plutonium(IV)−HCl solution to a TBA chloride solution in 4 M HCl, suggesting that the salt **2** is relatively soluble in HCl. However, subsequent evaporation of the reaction solution to near-dryness resulted in the isolation of $[n\text{-Bu}_4N]_2[PuCl_6]$ in 94% yield (Figure 3). Single-crystal X-ray diffraction data on **2** reveals that the Pu^{IV} center has a coordination number of 6 and is bound to

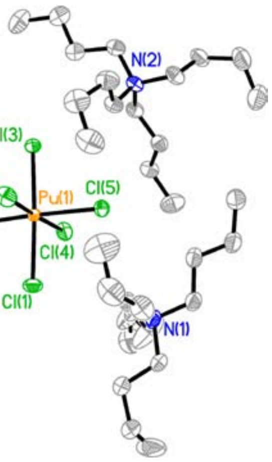

Figure 3. Thermal ellipsoid plot (50% probability level) of the structure of **2**. The H atoms have been omitted for clarity.

the Cl^- anions in a distorted octahedral geometry. As with **1**, there are no lattice solvent molecules. The Pu−Cl distances range from 2.5717(12) to 2.6026(11) Å and are consistent with those recently reported in $[PPh_4]_2[PuCl_6]$, which itself was part of a comparative study across $[AnCl_6]^{2-}$ anions.[4d] The "octahedral" Cl−Pu−Cl angles range from 87.69(3) to 92.11(4)° (Table 2).

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2

Pu(1)−Cl(1)	2.5993(11)	Pu(1)−Cl(4)	2.6026(11)
Pu(1)−Cl(2)	2.5717(12)	Pu(1)−Cl(5)	2.6008(11)
Pu(1)−Cl(3)	2.5936(11)	Pu(1)−Cl(6)	2.5957(11)
Cl(1)−Pu(1)−Cl(2)	88.72(4)	Cl(2)−Pu(1)−Cl(6)	92.11(4)
Cl(1)−Pu(1)−Cl(4)	91.55(4)	Cl(3)−Pu(1)−Cl(4)	91.11(4)
Cl(1)−Pu(1)−Cl(5)	89.81(3)	Cl(3)−Pu(1)−Cl(5)	91.79(3)
Cl(1)−Pu(1)−Cl(6)	87.69(3)	Cl(3)−Pu(1)−Cl(6)	90.73(3)
Cl(2)−Pu(1)−Cl(3)	88.71(4)	Cl(4)−Pu(1)−Cl(5)	88.30(3)
Cl(2)−Pu(1)−Cl(5)	88.24(4)	Cl(4)−Pu(1)−Cl(6)	91.36(4)

The vis−NIR spectrum of **2** dissolved in acetonitrile (Figure 4) resembles spectra attributed to the $[PuCl_6]^{2-}$ anion in 12 M HCl, MeCN, and other anhydrous solvents.[3c,4d,9] The solid-state diffuse-reflectance spectrum of pure compound **2** is also shown in Figure 4, and there is excellent correlation of the electronic transitions to the solution phase, supportive of identical speciation in both the solid state and solution. The Pu−Cl bond stretching vibration frequencies occur below 400 cm^{-1} and are outside the window of our IR spectroscopic measurements.

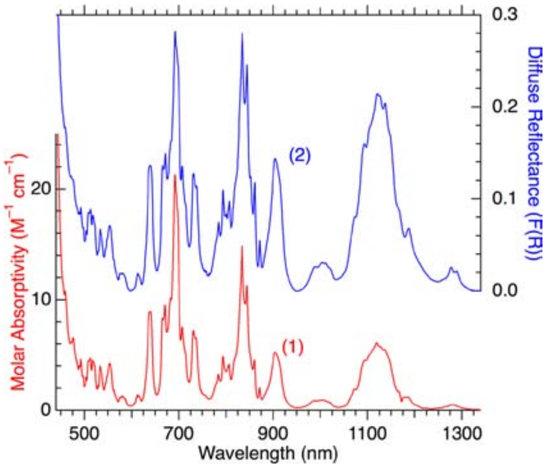

Figure 4. Solution electronic absorption spectrum of compound **2** dissolved in MeCN [red spectrum (1), left axis] and diffuse-reflectance spectrum of solid compound **2** [blue spectrum (2), right axis].

In summary, compounds **1** and **2** were prepared in high yields and were fully characterized. We have already begun to make use of compound **1** as a starting material in subsequent plutonium−ligand complexation studies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental details, crystal data and CIF files, and vis−NIR, IR, and Raman spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: gaunt@lanl.gov.

Notes

The authors declare no competing financial interest.

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(8) MeCN used in these experiments was not anhydrous, so the $[Pu(NO_3)_6]^{2-}$ anion is stable in the presence of trace water. However, when an aqueous plutonium(IV)−HNO_3 solution was added to MeCN, the resulting spectrum is not the same as the spectrum in Figure 2, suggesting other Pu(IV) nitrate species are present.

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