

Low-Valent Molecular Plutonium Halide Complexes

Andrew J. Gaunt,* Sean D. Reilly, Alejandro E. Enriquez, Trevor W. Hayton, James M. Boncella, Brian L. Scott, and Mary P. Neu*

Chemistry, Plutonium Manufacturing and Technology, and Materials Physics and Applications Divisions, and Associate Directorate for Chemistry, Life and Earth Sciences, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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Treatment of plutonium metal with 1.5 equiv of bromine in tetrahydrofuran (thf) led to isolation of $\text{PuBr}_3(\text{thf})_4$ (**1**), which is a new versatile synthon for exploration of non-aqueous Pu(III) chemistry. Adventitious water in the system resulted in structural characterization of the eight-coordinate complex $[\text{PuBr}_2(\text{H}_2\text{O})_6][\text{Br}]$ (**2**). The crystal structure of $\text{Pu}_3(\text{thf})_4$ (**3**) has been determined for the first time and is isostructural with $\text{U}_3(\text{thf})_4$. Attempts to form a bis(imido) plutonyl(VI) moiety ($[\text{Pu}(\text{NR})_2]^{2+}$) by oxidation of $\text{Pu}_3(\text{py})_4$ with iodine and $^t\text{BuNH}_2$ resulted in crystallization of the Pu(III) complex $[\text{Pu}_2(\text{thf})_4(\text{py})][\text{I}_3]$ (**4**). Dissolution of a Pu(IV) carbonate with a $\text{HCl}/\text{Et}_2\text{O}$ solution in thf gave the mixed valent (III/IV) complex salt $[\text{PuCl}_2(\text{thf})_5][\text{PuCl}_5(\text{thf})]$ (**5**) as the only tractable product. Oxidation of $\text{Pu}[\text{N}(\text{SiMe}_3)_2]_3$ with TeCl_4 afforded the Pu(IV) complex $\text{Pu}[\text{N}(\text{SiMe}_3)_2]_3\text{Cl}$ (**6**), which may prove to be a useful entry route for investigation of organometallic/non-aqueous tetravalent plutonium chemistry.

Introduction

Over the past couple of decades, molecular uranium chemistry has seen a renaissance that has challenged and evolved our understanding of the electronic structure, bonding, and reactivity of this early actinide element.^{1–3} However, similar extensive advances in transuranic chemistry have not yet occurred.⁴ As the inorganic chemistry community learns more about uranium, the fundamental question arises: how does the actinide contraction affect the reaction chemistry and bonding as the ions become smaller and have a greater effective nuclear charge from left to right across the 5f series?

An(III) ions become the predominant stable oxidation state beyond Am and are considered lanthanide-like in their behavior and chemical properties. It is also generally accepted that the potential for covalent interactions decreases and ionic bonding dominates moving from left to right across the 5f series. However, the exact details of the bonding and reactivity differences are unknown because the molecular structural and coordination chemistry has not been studied in as much depth as for uranium. Given the surprising reaction chemistry discovered for uranium, it is injudicious to make definitive assumptions about the chemical properties and reactivity of the transuranic elements unless those assumptions are validated through experiment as far as possible.

One indicator of how fundamental coordination chemistry knowledge decreases across the 5f series is to compare the number of entries in the Cambridge Structural Database.⁵ At the time of writing, for U there are 2228 entries, for Np there are 92, for Pu there are 31, for Am there are 7 and for Cm there are only 3 entries. This decrease is directly correlated with the increase in the radiological hazards associated with handling the isotopes and the reduced availability of suitable forms of the isotopes. However, with appropriate radiological facilities and access to suitable

* To whom correspondence should be addressed. E-mail: gaunt@lanl.gov (A.J.G.), mneu@lanl.gov (M.P.N.). Fax: 505-667-9905. Phone: 505-667-3395.

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(5) Information about the Cambridge Structural Database can be found at <http://www.ccdc.cam.ac.uk/products/csd/>.

precursors, it is feasible to conduct coordination chemistry studies, to some extent, with a number of the transuranic elements (mainly Np–Cm). In addition to scientific curiosity to understand the chemistry of all of the elements in the periodic table, obtaining a comprehensive grasp of the fundamental chemical properties of the transuranic elements is vital to support the development of Advanced Nuclear Fuel Cycles, waste remediation technologies, and to be able to accurately predict environmental mobility of Pu under a wide range of conditions. In particular, understanding the extent to which covalency is important in actinide bonding (and how it differs compared to lanthanide bonding) with soft donor ligands provides the fundamental principles that can be used to develop An(III)/Ln(III) separations that are integral to proposed partitioning and transmutation processes.^{6–22} The majority of air and water stable ligands are hard donors and form actinide complexes in which the bonding is predominately ionic. To be able to fully probe covalent interactions, non-aqueous systems must be studied with ligand sets chosen to invoke some degree of orbital overlap in the bonding. In our laboratory, we have developed the capability to perform coordination chemistry studies with Pu in non-aqueous, inert atmospheric environments.

One of the challenges in the development of molecular plutonium (and other transuranic elements) chemistry, specifically in non-aqueous environments, is to establish a range of suitable precursors to allow synthetic access to target complexes. To the best of our knowledge, only three trivalent and one tetravalent non-aqueous complex of Pu, with potential for wide-ranging synthetic utility, have been reported. The Pu(III) complexes, PuI₃(thf)₄, PuI₃(py)₄, and Pu[N(SiMe₃)₂]₃, were synthesized in 1994 but their crystal structures were not determined²³ (although we have recently

communicated the crystal structure of Pu[N(SiMe₃)₂]₃).²⁴ The Pu(IV) complex anion, [PuCl₆]^{2–}, has been prepared and characterized as various salts.^{25–28} We are seeking to synthesize new Pu precursors soluble in organic solvents and to begin to develop their reaction chemistry with non-aqueous and organometallic-type ligands that will provide insight into the fundamental electronic, bonding, and structural properties of Pu.

Here, we report the synthesis and characterization of PuBr₃(thf)₄ (**1**), a new synthon for Pu(III) chemistry, and the crystal structure of the previously reported PuI₃(thf)₄ (**3**) is determined for the first time. We report the syntheses of Pu[N(SiMe₃)₂]₃Cl (**6**), which is the first structurally characterized neutral, organic soluble Pu(IV) molecule from an oxygen and moisture free environment. We also provide structural characterization of [PuBr₂(H₂O)₆][Br] (**2**), [PuI₂(thf)₄(py)][I₃] (**4**), and the mixed III/IV complex salt [PuCl₂(thf)₅][PuCl₅(thf)] (**5**), which were all obtained as unintended products in our pursuit of other molecular Pu compounds.

Experimental Section

General Information. Caution! ²³⁹Pu is a high specific-activity α -particle emitting radionuclide. This research was conducted in a radiological facility with appropriate analyses of hazards and implementation of controls for the safe handling and manipulation of radioactive materials.

α -Phase plutonium metal pieces of weapons-grade isotopic composition and aqueous Pu stocks were obtained internally from Los Alamos National Laboratory. All reactions were performed in an MBraun Labmaster 130 Helium atmosphere drybox (except the preparation of Pu(IV)-carbonate). Hexanes, toluene, and tetrahydrofuran (thf) were dried with the use of activated alumina columns (A2, 12 32, Purify). Other solvents were purchased in anhydrous grade from Aldrich. All solvents were stored over a 1:1 mixture of 3 Å and 4 Å molecular sieves before use. All ¹H NMR spectra were referenced to residual protio resonances and were obtained on samples in 4 mm Teflon NMR tube liners inserted into 5 mm NMR tubes to multiply contain the radioactive samples. NMR spectra were recorded at ambient temperature on a Bruker Avance 300 MHz spectrometer. Electronic absorption spectra were recorded on a Varian Cary 6000i UV/vis/nIR spectrophotometer.

PuBr₃(thf)₄ (1**).** Pu metal (0.0181 g, 0.0757 mmol) suspended in thf (3 cm³) was treated with a solution of Br₂ (0.12 cm³ of 0.954 M Br₂ in thf solution, 0.114 mmol), and the mixture was stirred at ambient temperature for 4 days. The resulting blue solution was filtered through a glass fiber circle to remove unreacted Pu metal. Hexanes (15 cm³) was added to the filtrate causing a precipitate that was collected, washed with hexanes, and dried in vacuo to give a light blue powder (0.0311 g, 54% yield). Single crystals suitable for X-ray diffraction were obtained from a thf solution of **1** stored at –35 °C for several days (crystals appeared lavender in color under the microscope, but blue to the naked eye).

¹H NMR (thf-d₈): δ 3.58(s), 1.73(s) (free thf); 3.62(m), 1.78(m) (coordinated thf). UV/vis/nIR (solution of **1** in thf) (λ_{\max} , nm): 245,

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312, 338, 364, 427, 454, 462, 513, 569, 584, 613, 671, 780, 808(sh), 826(sh), 906, 915(sh), 1028, 1110, 1137(sh), 1402, 1550.

[PuBr₂(H₂O)₆][Br] (2). As for **1**, except after crystallization of the product, it was washed with CH₂Cl₂ (2 cm³). The crystals were partially redissolved in thf, and the mixture placed in the freezer. After 2 days at -35 °C, both lavender and blue colored crystals were deposited. A blue single crystal was selected for X-ray diffraction analysis and determined to be **2**.

PuI₃(thf)₄ (3). Prepared according to the literature.²³ X-ray diffraction quality crystals of **3** were obtained from powdered **3** (off-white color) dissolved in thf and stored at -35 °C for several days to give pale pink blocks.

[PuI₂(thf)₄(py)] [I₃] (4). ¹BuNH₂ in thf (0.140 cm³, 0.72 M, 0.10 mmol) was added to PuI₃(py)₄²³ (0.0153 g, 0.016 mmol) in thf (3 cm³) followed by addition of I₂ (0.0062 g, 0.024 mmol). The mixture was stirred at room temperature. After 10 min an orange solution and a small amount of yellow precipitate had formed. The solution was filtered and the solvent removed in vacuo. Toluene (3 cm³) was added to the residue to give an orange solution that was filtered and stored at -35 °C. A few orange needles (0.0039 g) of single-crystal X-ray diffraction quality were deposited after 3 days.

[PuCl₂(thf)₅][PuCl₅(thf)] (5). Green crystals of Pu(IV)-carbonate (presumed to be Na₆Pu(CO₃)₅)²⁹ were prepared by adding a solution of Pu(IV) in HCl (0.15 cm³, 0.51 M Pu, 2–4 M HCl) to a rapidly stirred 3 M Na₂CO₃ solution (0.40 cm³), followed by evaporation for several days. The Pu(IV) carbonate crystals were suspended in thf (2 cm³) and excess HCl in Et₂O (1 M, 2 cm³) added resulting in a yellow solution and a white precipitate. The solution was filtered and a few drops of TMSCl were added to remove any residual water. Hexanes (10 cm³) were added to the solution with stirring. After storage at -35 °C overnight, a yellow powder formed that was dried in vacuo (0.0055 g). Dissolution of the powder in thf (1 cm³), filtration, and vapor diffusion with n-pentane gave a few yellow single-crystals of X-ray diffraction quality.

A few crystals of **5** that were yellow/red in appearance were also obtained from the hexanes washings of the solid Pu(VI) complex [PuO₂Cl₂(thf)₂]₂³⁰ stored at ambient temperature for 4 weeks.

UV/vis/nIR (solution of **5** in thf) (λ_{max} , nm): 245, 305, 328(sh), 353(sh), 396(sh), 535, 547, 564, 585, 610, 644, 659, 669, 687, 702, 757, 818(sh), 822, 863, 905, 924, 952, 1023, 1030(sh), 1083(sh), 1108, 1146, 1386.

Pu[N(SiMe₃)₂]₃Cl (6). Pu[N(SiMe₃)₂]₃²⁴ (0.0257 g, 0.036 mmol) was dissolved in toluene (3 cm³) and solid TeCl₄ (0.0024 g, 0.0090 mmol) was added to the orange solution. The TeCl₄ dissolved over a few seconds resulting in a color change to a dark brown solution, which was stirred at ambient temperature for 4 h. The solution was filtered and the volume of the filtrate was reduced in vacuo to 1 cm³ and then stored at -35 °C, resulting in crystalline blocks after several days (0.0106 g, 39% yield).

¹H NMR (toluene-d₈): δ -1.59.

UV/vis/nIR (solution of **6** in toluene) (λ_{max} , nm): 293, 347, 416, 454(sh), 482(sh), 534(sh), 552(sh), 598(sh), 687, 703, 717, 726, 732, 773, 799, 817, 872, 888, 1109, 1129(sh), 1189, 1296(br).

Crystallographic Data Collection and Refinement. Inside the inert atmosphere glovebox, crystals of **1–6** were coated with Paratone-N and then mounted inside a 0.5 mm capillary. The capillaries were sealed with wax and their external surfaces were

coated with a thin film of acrylic dissolved in ethyl acetate ("Hard as Nails" nail polish) to provide appropriate containment of the radioactive material. The data for **1–5** were collected on a Bruker SMART APEX II charge-coupled-device (CCD) diffractometer. For these crystals, a hemisphere of data was collected using ω scans, with 5 s frame exposures and 0.5° frame widths. Data collection and initial indexing and cell refinement were handled using the APEX II³¹ software. Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using the SAINT+³² software.

X-ray data for **6** were collected on a SMART 1k diffractometer. A hemisphere of data was collected using ϕ scans, with 10 s frame exposures and 0.5° frame widths. Data collection and initial indexing and cell refinement were handled using the SMART³³ software. Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using the SAINT³⁴ software.

Both X-ray instruments were equipped with graphite monochromatized Mo K α X-ray source ($\lambda = 0.71073$ Å), and MonoCap X-ray source optics. All data collections employed a Bruker Kyro-Flex liquid nitrogen vapor cooling device with the data collection temperature set at 141(2) K. For all crystals the data were corrected for absorption using the SADABS³⁵ program. Decay of reflection intensity was monitored via analysis of redundant frames. The structures were solved using Direct methods and difference Fourier techniques. All hydrogen atom positions were idealized, and rode on the atom to which they were attached (except **2**, for which hydrogen atom positions were found and refined with temperature factors set to 0.08 Å²). Final refinements include anisotropic temperature factors on all non-hydrogen atoms. For all structures, structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.³⁶ Additional data collection and refinement parameters are given in Table 1.

Results and Discussion

PuBr₃(thf)₄ (1). Oxidation of Pu metal with 1.5 equiv of bromine in thf (Scheme 1) afforded the Pu(III) tribromide salt **1** (see Figure 1 and Table 2). The crystal structure of **1** has the same atomic connectivity as in UI₃(thf)₄²³ and consists of a central Pu atom in a geometry best described as distorted pentagonal bipyramidal. Two Br atoms occupy the axial positions and the equatorial plane consists of one Br atom and the four O atoms of the coordinated thf molecules. The average Pu–Br distance is 2.8679(11) Å and the average Pu–O distance is 2.502(6) Å. The equatorial Br ion forces the axial Br ions to bend away from linearity with a Br–Pu–Br angle of 164.960(17)°, which is a larger distortion than in UI₃(thf)₄ for which the corresponding angle is 171.3(5)°. On the basis of ionic radii, Ce is an appropriate lanthanide ion to compare to Pu.³⁷ The crystal structure of CeBr₃(thf)₄ is isostructural with **1**, and the average Ce–Br distance is 2.8940(15) Å,³⁸ which is longer than the average Pu–Br distance in **1** by 0.0261 Å. The axial Br–Ce–Br angle in CeBr₃(thf)₄ is 166.11(3)°, which is similar to the

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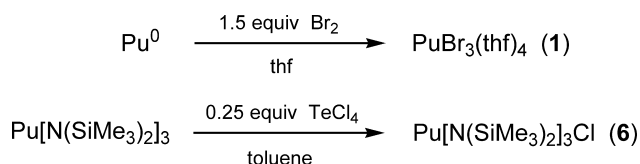
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Table 1. Selected Crystallographic Data for **1-6**

	compound					
	1	2	3	4	5	6
empirical formula	C ₁₆ H ₃₂ Br ₃ O ₄ Pu	H ₁₂ Br ₃ O ₆ Pu	C ₁₆ H ₃₂ I ₃ O ₄ Pu	C ₂₁ H ₃₇ I ₅ NO ₄ Pu	C ₂₄ H ₄₈ Cl ₇ O ₆ Pu ₂	C ₁₈ H ₅₄ PuClN ₃ Si ₆
fw	767.14	586.80	908.14	1241.05	1158.81	755.61
crystal system	triclinic	monoclinic	monoclinic	orthorhombic	monoclinic	trigonal
space group	<i>P</i> $\bar{1}$	<i>P2</i> / <i>n</i>	<i>P2</i> ₁ / <i>c</i>	<i>Pbcn</i>	<i>P2</i> / <i>c</i>	<i>R3c</i>
<i>a</i> (Å)	8.1698(12)	8.2148(10)	8.6621(9)	12.6162(13)	12.1865(17)	18.396(2)
<i>b</i> (Å)	9.3859(14)	6.7824(8)	17.2509(18)	22.066(2)	11.1628(15)	18.396(2)
<i>c</i> (Å)	15.414(2)	10.0325(12)	16.5314(17)	11.8472(12)	13.9197(19)	16.871(4)
α (°)	78.526(2)	90.00	90.00	90.00	90.00	90.00
β (°)	86.813(2)	93.7760(10)	92.8190(10)	90.00	104.186(2)	90.00
γ (°)	74.934(2)	90.00	90.00	90.00	90.00	120.00
<i>V</i> (Å ³)	1118.5(3)	557.76(12)	2467.3(4)	3298.1(6)	1835.8(4)	4944.7(15)
<i>Z</i>	2	2	4	4	2	6
μ (mm ⁻¹)	8.321	16.639	6.440	6.703	4.101	2.310
<i>D</i> _{calc} (g/cm ³)	2.287	3.512	2.453	2.505	2.107	1.529
<i>R</i> ₁	0.0286	0.0181	0.0322	0.0355	0.0432	0.0540
<i>wR</i> ₂	0.0633	0.0467	0.0584	0.0911	0.0782	0.0912

Scheme 1. Synthetic Routes to PuBr₃(thf)₄ (**1**) and Pu[N(SiMe₃)₂]₃Cl (**6**) Molecular Complexes, Which Have Potential Utility as Versatile Precursors for Pu(III) and Pu(IV) Non-Aqueous/Organometallic Chemistry, Respectively



corresponding angle in **1**. The synthesis of UBr₃(thf)₄ has been reported in the literature, but its crystal structure was not determined.²³

The ¹H NMR of **1** in thf-d₈ reveals resonances for coordinated and uncoordinated thf molecules. Pu(III) has a 5f⁵ configuration and the UV/vis/nIR electronic absorption spectrum of **1** dissolved in thf contains f-f transitions and f-d transitions as expected. Compound **1** is a new molecular

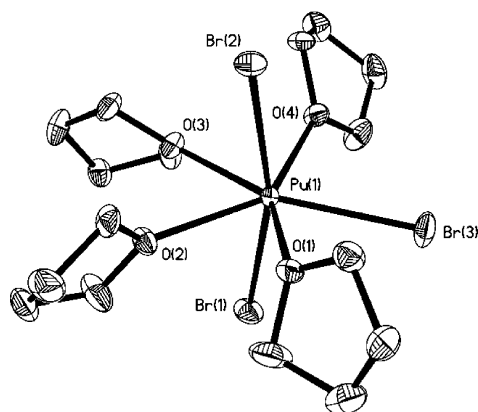


Figure 1. Thermal ellipsoid plot (50% probability) of the crystal structure of compound **1**. The H atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Pu(1)–O(1)	2.479(3)	Pu(1)–Br(1)	2.8746(6)
Pu(1)–O(2)	2.541(3)	Pu(1)–Br(2)	2.8511(6)
Pu(1)–O(3)	2.504(3)	Pu(1)–Br(3)	2.8781(7)
Pu(1)–O(4)	2.483(3)		
Br(1)–Pu(1)–Br(2)	164.960(17)	Br(2)–Pu(1)–Br(3)	106.049(17)
Br(1)–Pu(1)–Br(3)	88.991(17)	O(1)–Pu(1)–Br(3)	75.76(8)
Br(3)–Pu(1)–O(4)	77.30(8)	O(3)–Pu(1)–O(4)	69.65(11)
O(2)–Pu(1)–O(3)	72.01(11)	O(1)–Pu(1)–O(2)	68.20(11)

precursor for Pu(III) non-aqueous chemistry and should readily undergo metathesis and Lewis-base displacement reactions.

[PuBr₂(H₂O)₆][Br] (2). In one attempted oxidation of Pu metal with bromine in thf, the presence of adventitious water in the system (probably as an impurity in CH₂Cl₂) led to the unintended isolation of **2** (see Figure 2 and Table 3). The crystal structure of **2** comprises a complex cation of Pu, with two coordinated Br ions and six coordinated water molecules. The charge is balanced by an outer-sphere Br ion. According to Haigh's criteria,³⁹ the geometry about the Pu center is best described as distorted square antiprismatic. The Pu–Br distance for the coordinated Br ions is 2.9771(5) Å, slightly longer than the average Pu–Br distance in **1**, probably reflecting the overall increase in coordination number from seven in **1** to eight in **2**. The average Pu–O distance in **2** is 2.472(5) Å. For comparison, the plutonium aquo bond distances in [Pu(H₂O)₉][CF₃SO₃]₃,⁴⁰ in which the Pu atom has a tricapped trigonal prismatic geometry, are Pu–O(capping) at 2.574(3) Å and Pu–O(prismatic) at 2.476(2) Å. The reason for the outer-sphere Br anion in **2** is not clear but may be a

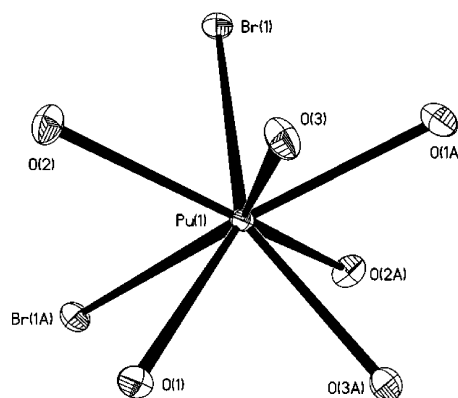


Figure 2. Thermal ellipsoid plot (50% probability) of the crystal structure of compound **2**. The H atoms and Br outer-sphere anion have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **2**

Pu(1)–O(1)	2.480(3)	Pu(1)–O(3)	2.454(3)
Pu(1)–O(2)	2.483(3)	Pu(1)–Br(1)	2.9771(5)
Br(1)–Pu(1)–Br(1A)	84.64(2)		

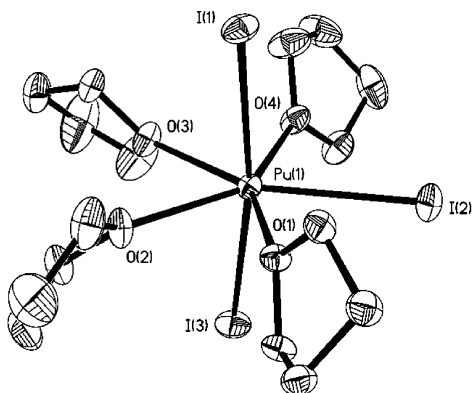


Figure 3. Thermal ellipsoid plot (50% probability) of the crystal structure of compound **3**. The H atoms have been omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **3**

Pu(1)–O(1)	2.445(3)	Pu(1)–I(1)	3.0727(5)
Pu(1)–O(2)	2.521(4)	Pu(1)–I(2)	3.1342(5)
Pu(1)–O(3)	2.495(4)	Pu(1)–I(3)	3.0937(5)
Pu(1)–O(4)	2.476(4)		
I(1)–Pu(1)–I(3)	171.162(12)	I(2)–Pu(1)–I(3)	94.059(13)
I(1)–Pu(1)–I(2)	94.749(12)	O(1)–Pu(1)–I(2)	73.78(8)
I(2)–Pu(1)–O(4)	76.18(9)	O(3)–Pu(1)–O(4)	69.79(12)
O(2)–Pu(1)–O(3)	70.41(12)	O(1)–Pu(1)–O(2)	70.13(12)

reflection of the relatively soft nature of the Br anions and effective competition from the hard O-donor water molecules (also see discussion of **4** and **5** for references to autoionization in lanthanide complexes). Surprisingly there are no reported structures of molecular Pu bromides, either aqueous or non-aqueous, for comparison with the Pu–Br distances in **2** (except for complex **1** reported herein).

PuI₃(thf)₄ (3). The synthesis and spectroscopic characterization of **3** has been reported previously but the molecular crystal structure was not determined.²³ We decided to repeat the synthesis to determine if the structure of **3** was identical to its U analogue. This was a useful task not only to help identify and build up our knowledge of structural preferences and trends in non-aqueous molecular Pu complexes but also because workers from this institution had previously obtained a poor quality crystal structure (unpublished) of [Pu₂(thf)₅][I₃] via a very similar synthetic route. Therefore, confirmation that crystallization of the reported PuI₃(thf)₄ does form the neutral complex and not a complex cation is of value.

The crystal structure of **3** is indeed isostructural with the U analogue (see Figure 3 and Table 4). The Pu center adopts a distorted pentagonal bipyramidal geometry with two iodides in the axial positions, while the equatorial plane contains the third iodide and the four O atoms of the thf molecules. The average Pu–I distance is 3.1002(9) Å and the average Pu–O distance is 2.484(8) Å compared to 3.130(3) and 2.52(2) Å, respectively, in UI₃(thf)₄.²³ The axial I–Pu–I angle is 171.162(12)° and is similar to the corresponding angle in UI₃(thf)₄ of 171.3(5)°. The average Ce–I distance

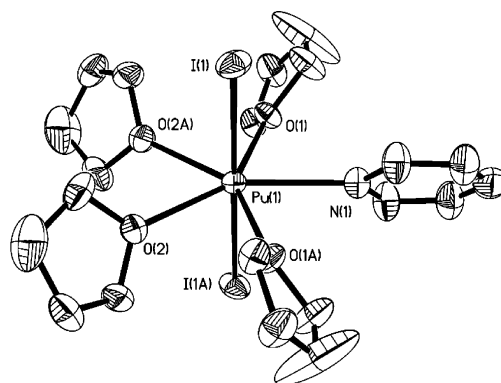


Figure 4. Thermal ellipsoid plot (50% probability) of the crystal structure of compound **4**. The H atoms and the outer-sphere [I₃][−] anion have been omitted for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **4**

Pu(1)–I(1)	3.0721(5)	Pu(1)–N(1)	2.596(7)
Pu(1)–O(1)	2.462(5)	I(2)–I(3)	2.9113(6)
Pu(1)–O(2)	2.486(4)		
I(1)–Pu(1)–I(1A)	179.79(2)	I(2)–I(3)–I(2)	180.0
N(1)–Pu(1)–O(1)	72.55(10)	O(1)–Pu(1)–O(2A)	71.50(15)
O(1A)–Pu(1)–O(2)	71.50(15)	N(1)–Pu(1)–O(1A)	72.55(10)
O(2)–Pu(1)–O(2A)	71.9(2)		

in CeI₃(thf)₄ is 3.141(3) Å⁴¹ and is longer than the average Pu–I distance in **3**, as is the average Ce–O distance of 2.515(6) Å compared to the average Pu–O distance in **3**. The axial I–Ce–I angle is 171.525(12) and is comparable to the corresponding angle in **3**.

[PuI₂(thf)₄(py)][I₃] (4). The imido analogue of the uranyl(VI) dioxo cation, [U(NR)₂]²⁺, was recently synthesized for the first time through oxidation of U metal by 3 equiv of iodine in the presence of 6 equiv of ^tBuNH₂.⁴² The isolation of the uranyl bis-imido complex raises the possibility of generating the Np, Pu, and Am analogues. However, we found that oxidation of Pu metal with 3 equiv of iodine and 6 equiv of ^tBuNH₂ did not lead to isolation of a Pu(VI) bis(imido) moiety. An alternative synthesis using PuI₃(py)₄ as the precursor led to **4** as the only isolable product (see Figure 4 and Table 5). The crystal structure of **4** contains the [PuI₂(thf)₄(py)]⁺ cation, in which the Pu center has a distorted pentagonal bipyramidal geometry with the iodide ions in the axial positions and the 4 O atoms (thf) and the N atom (pyridine) in the equatorial plane. The Pu–I distance is 3.0721(5) Å and is shorter than the average Pu–I distance in **3** probably because only two iodides are directly coordinated to the Pu ion in **4**. The I–Pu–I angle is 179.79(2)° and more closely approximates a regular pentagonal bipyramid than **3** which exhibits a more bent axial I–Pu–I angle of 171.162(12)°. The pyridine molecule is coordinated with a Pu–N distance of 2.596(7) Å, and the bound thf molecules have an average Pu–O distance of 2.474(6) Å. The charge is balanced by the [I₃][−] anion, in which the I–I distance is 2.9113(6) Å and the I–I–I angle is 180.0°. The [I₃][−] anion is likely formed because of the excess iodine present in the system. The formation of the [I₃][−] anion is not often produced

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in uranium chemistry because excess iodine will often result in oxidation of U(III) to U(IV), although it has been observed in uranium phthalocyanines,^{43–45} $[\text{UO}_2(\text{OPPh}_3)_4][\text{I}_3]_2$,⁴⁶ and $[\text{UO}_2(\text{tdpo})_4][\text{I}_3]_2$.⁴⁷ The isolation of neutral organic solvates of f-element ions is not always straightforward, and the $[\text{I}_3]^-$ anion or autoionization has been shown to occur in lanthanide chemistry.^{48–53} $[\text{LnI}_2(\text{thf})_5][\text{LnI}_4(\text{thf})_2]$ (Ln = Sm, Yb)^{48,49} and $[\text{LnI}_2(\text{py})_5][\text{I}]$ (Ln = Yb, Lu)^{50,51} are known. $[\text{LnI}_2(\text{thf})_5][\text{I}_3]$ (Ln = La, Yb)^{51,52} are isostructural with **4** and were both formed despite there being no excess iodine present in the system (1.5 equiv was used to oxidize Ln⁰).

The reason for the failure to form the hexavalent $[\text{Pu}(=\text{N}^t\text{Bu})_2]^{2+}$ ion is likely a result of the actinide contraction. As one proceeds across the 5f series the trivalent oxidation state becomes predominant and the ions have a higher charge density. It appears that, under the conditions studied, the energetic driving force for the formation of $[\text{Pu}(=\text{N}^t\text{Bu})_2]^{2+}$ is insufficient to overcome the energy required for oxidation beyond Pu(III) (and/or that a significantly stronger oxidant is required). Other attempts to prepare the plutonyl bis(imido) ion by changing solvent and precursor were equally unsuccessful. Because Np sits between U and Pu in the actinide series, the neptunyl bis(imido) analogue may be stable and isolable. However, Np metal is not readily available, and there is little information detailing alternative routes to the low valent anhydrous precursors that would be required for the synthesis of $[\text{Np}(=\text{N}^t\text{Bu})_2]^{2+}$ or $[\text{Np}(=\text{N}^t\text{Bu})_2]^+$. Facile syntheses of Np precursors similar to **1** and **3** (preferably without the need for Np metal or an anhydrous Np(III) halide) would greatly aid development of non-aqueous Np chemistry. Ideally, future synthetic routes to Np(III) precursors will develop a method to isolate an organic-soluble anhydrous molecule starting from NpO_2 or an aqueous solution, which are much easier to obtain than other forms of Np. We have found this methodology successful for preparing a non-aqueous plutonyl(VI) precursor.³⁰

[PuCl₂(thf)₅][PuCl₅(thf)] (5). Considering the above-mentioned difficulty in oxidizing Pu beyond Pu(III) and the failure so far to isolate a Pu(VI) bis(imido) ion, we looked for alternative routes to generate non-aqueous synthons of Pu in higher oxidation states. We recently communicated the synthesis and characterization of $[\text{PuO}_2\text{Cl}_2(\text{thf})_2]_2$,³⁰

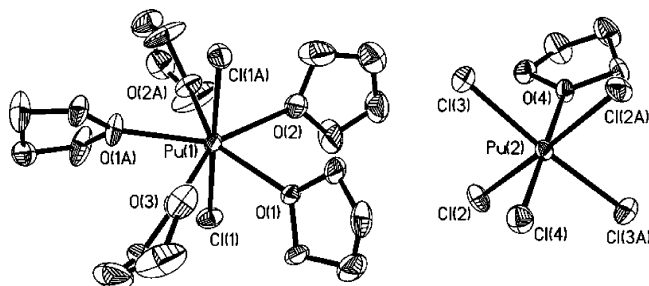


Figure 5. Thermal ellipsoid plot (50% probability) of the crystal structure of compound **5**. The Pu(IV) anion is on the right and the Pu(III) cation is on the left. The H atoms have been omitted for clarity.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **5**

Pu(1)–Cl(1)	2.6771(19)	Cl(1)–Pu(1)–Cl(1A)	176.36(8)
Pu(1)–O(1)	2.462(5)	O(1)–Pu(1)–O(2)	71.96(17)
Pu(1)–O(2)	2.478(5)	O(1)–Pu(1)–O(3)	72.02(12)
Pu(1)–O(3)	2.451(6)	O(1A)–Pu(1)–O(3)	72.02(12)
		O(1A)–Pu(1)–O(2A)	71.96(17)
		O(2)–Pu(1)–O(2A)	73.4(3)
Pu(2)–O(4)	2.417(6)	O(4)–Pu(2)–Cl(2)	86.76(4)
Pu(2)–Cl(2)	2.5664(18)	O(4)–Pu(2)–Cl(3)	86.42(4)
Pu(2)–Cl(3)	2.577(3)	O(4)–Pu(2)–Cl(4)	180.0
Pu(2)–Cl(4)	2.541(3)		

which was the first example of a non-aqueous synthon suitable for investigation of the Pu(VI) plutonyl dioxo cation. The Pu(VI) complex was synthesized by dissolution of PuO_2CO_3 by HCl in thf. The success of that reaction posed the question: Can dissolution of anhydrous carbonates provide facile routes to organic-soluble neutral halide complexes of other oxidation states of Pu, specifically Pu(IV)? There are no single crystal structures of $\text{PuX}_4(\text{sol})_y$ (X = halide, sol = coordinating organic solvent) molecules, although the Lewis base adducts $\text{PuCl}_4(\text{dmf})_{2.5}$, $\text{PuCl}_4(\text{dipa})_2$, $\text{PuCl}_4(\text{dippa})_2$, $\text{PuCl}_4(\text{tibpo})_2$, $\text{PuCl}_4(\text{dmppo})_2$, and $\text{PuCl}_4(\text{mdppo})_3$ (dmf = $\text{HCON}(\text{CH}_3)_2$, dipa = $\text{CH}_3\text{CON}(i\text{-C}_3\text{H}_7)_2$, dippa = $(\text{C}_2\text{H}_5)\text{CON}(i\text{-CH}_3\text{H}_7)_2$, tibpo = $\text{P}(i\text{-C}_4\text{H}_9)_3\text{O}$, dmppo = $\text{P}(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{O}$, mdppo = $\text{P}(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{O}$) have been synthesized but not structurally characterized.⁵⁴

Dissolution of Pu(IV) carbonate with HCl in thf led to a green solution. The only identifiable product isolated from the solution were a few crystals of a mixed-valent Pu(III)/Pu(IV) complex salt **5** (see Figure 5 and Table 6). Crystals of **5** were also obtained from the hexanes washings of the solid Pu(VI) complex $[\text{PuO}_2\text{Cl}_2(\text{thf})_2]_2$ stored at ambient temperature for 4 weeks. It is known that Pu(VI) undergoes reduction to Pu(V) followed by disproportionation to Pu(IV) and Pu(VI), but the formation of **5** that contains a Pu(III) ion highlights the apparent preference for low valent oxidation states of Pu under inert atmospheric conditions in organic solvents (at least for the systems that we have studied).

The structure of the Pu(III) cation in **5**, $[\text{PuCl}_2(\text{thf})_5]^+$, has the Cl ions located in the axial positions and the O atoms of the thf molecules in the equatorial positions of the distorted pentagonal bipyramidal geometry around the Pu center. The Pu–Cl distance is 2.6771(19) Å, with a Cl–Pu–Cl angle of 176.36(8)°, and the average Pu–O distance is 2.464(9) Å. The Pu(IV) anion in **5**, $[\text{PuCl}_5(\text{thf})]^-$, has a distorted

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octahedral geometry around the Pu center. The average Pu–Cl distance is 2.561(5) Å and the Pu–O distance is 2.417(6) Å, which are shorter than in the Pu(III) cation as is expected as a result of the smaller ionic radius of Pu(IV) compared to Pu(III).

Although there are no other examples of non-aqueous Lewis-base adducts of Pu(III) chlorides, the full single crystal structures of the aqueous Pu(III) chlorides, $\text{Cs}[\text{PuCl}_4(\text{H}_2\text{O})_4]$, $\text{Cs}_5[\text{PuCl}_4(\text{H}_2\text{O})_4]\text{Cl}_4 \cdot 2\text{H}_2\text{O}$, and $(\text{Et}_4\text{N})[\text{PuCl}_2(\text{H}_2\text{O})_6]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ have been determined.⁵⁵ In striking contrast with our non-aqueous focused work, Wilson and co-workers noted the difficulty posed in maintaining Pu(III) in the reduced state and the requirement for the presence of excess reducing agents in the system, such as hydroxylamine or hydrogen peroxide. Other fully structurally characterized Pu(III) chlorides are the extended solid state lattices PuCl_3 ,⁵⁶ K_2PuCl_5 ,⁵⁷ and Rb_2PuCl_5 .⁵⁷ A number of Pu(IV) chlorides (or molecules containing Pu–Cl bonds) have been reported, but to our knowledge full single-crystal structural characterizations are limited to $\text{Pu}(\text{POPO})(\text{NO}_3)_2\text{Cl}_2$ (POPO = 2,6-bis[(diphenylphosphino)-methyl]benzene P,P'-dioxide),⁵⁸ and the solid state structures Rb_2PuCl_6 ⁵⁹ and K_2PuCl_6 .⁵⁹ The Ce(III)/Ce(IV) analog of **5**, $[\text{CeCl}_2(\text{thf})_5][\text{CeCl}_5(\text{thf})]$,⁶⁰ is known as is the structurally similar complex $[\text{CeCl}(\text{NO}_3)(\text{thf})_5][\text{CeCl}_5(\text{thf})]$ ⁶¹ and were both formed through autoionization processes. We are currently studying the effects of changing the solvent environment and the identity of the anion to attempt to isolate a neutral organic solvate adduct of Pu(IV).

Pu[N(SiMe₃)₂]₃Cl (6). We have found that a number of oxidants have failed to oxidize Pu beyond Pu(III) to Pu(IV) or Pu(VI). Addition of excess Br₂ or I₂ to Pu metal only results in oxidation to Pu(III). We have also added [NO][BF₄] and TMS-N₃ to Pu(III) precursors and observed no oxidation. These findings are not easy to explain, especially given the ease with which Pu(IV) can be generated in aqueous solutions, and in fact being rather more stable than Pu(III) in most aqueous solutions. However, some comparisons can be drawn to cerium chemistry, in which similar peculiar observations have been reported. For instance, Br₂, I₂, NBS, NCS, AgBF₄, AgCN, Hg(C₆F₅)₂, PbCl₂, and ^tBuOO^tBu all failed to oxidize [Ce^{III}(NR₂)₃], yet TeCl₄ and PBr₂Ph₃ (that are, at least on paper, less powerful oxidants than molecular halogens) result in oxidation of Ce(III) to Ce(IV) to form [CeCl(NR₂)₃] and [CeBr(NR₂)₃], respectively.³⁸ It was speculated that the ability of TeCl₄ to oxidize the Ce(III) silylamide may, in part, be due to formation of [TeCl₃]⁺ ions in solution. As an attempt to isolate a Pu(IV) complex in our non-aqueous systems, and to determine if Pu(III) does mimic the behavior of Ce(III), we treated Pu[N(SiMe₃)₂]₃

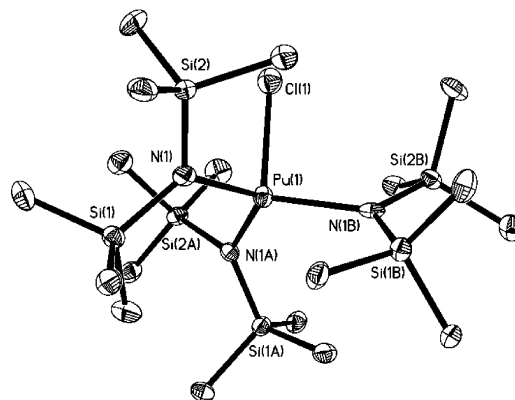


Figure 6. Thermal ellipsoid plot (50% probability) of the crystal structure of compound **6**. The H atoms have been omitted for clarity.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for **6**

Pu(1)–N(1)	2.207(6)	Cl(1)–Pu(1)–N(1)	99.9(1)
Pu(1)–Cl(1)	2.595(3)	N(1)–Pu(1)–N(1A)	117.1(1)

with 0.25 equiv of TeCl₄ (Scheme 1) and obtained the Pu(IV) compound **6** (see Figure 6 and Table 7).

The single crystal structure of **6** is isostructural with the Ce analogue with a geometry best described as a distorted tetrahedron. The Pu atom lies on a 3-fold symmetry axis providing equivalence to the Pu–N and N–Pu–N distances and angles, respectively. The Pu–N distance is 2.207(6) Å and the Pu–Cl distance is 2.595(3) Å. These distances compare to Ce–N and Ce–Cl lengths of 2.217(3) and 2.597(2) Å, respectively, in Ce[N(SiMe₃)₂]₃Cl.³⁸ The N(1)–Pu–Cl(1) and N(1)–Pu–N(1A) angles in **6** are 99.9(1) and 117.1(1)°, respectively, reflecting why a tetrahedral description of the geometry around the Pu center would not be appropriate. The corresponding angles in Ce[N(SiMe₃)₂]₃Cl are 99.48(7) and 117.34(4)°. The single resonance observed at –1.59 ppm in the ¹H NMR spectrum of **6** dissolved in toluene-*d*₈ is attributed to the silyl amide complex, although there is an unlikely possibility that this peak is due to the presence of “free” silyl amide (and the peak for the complex broadened into the baseline because of the proximity of the paramagnetic Pu(IV) ion).

Examples of full structural characterization of non-aqueous Pu(IV) molecules that would fall under the categories of soft-donor or organometallic complexes are limited to Pu(Et₂dtc)₄ (Et₂dtc[–] = N,N-diethyldithiocarbamate).^{62,63} Pu(IV)-COT (and substituted COT derivatives),^{64–68} Pu(IV)-Cp complexes,^{69–71} Cp₃Pu(NCS),⁶⁹ [AsPh₄][Pu(Cp)₃(NCS)],⁷² and Pu(BH₄)₄⁷³ have also been reported but with no single crystal structure data. Compound **6** should readily undergo both metathesis and deprotonation reactions to provide a route to

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Table 8. Comparison of Bond Distances (Å) and Angles (deg) (M = f-metal ion; X = halide) of **1** and **3** with Related Compounds in the Literature^a

	PuBr ₃ (thf) ₄ (1)	CeBr ₃ (thf) ₄ ³⁸	PuI ₃ (thf) ₄ (3)	CeI ₃ (thf) ₄ ⁴¹	UI ₃ (thf) ₄ ²³
M–X	2.8679(11)	2.8940(15)	3.1002(9)	3.141(3)	3.130(3)
X–M–X (axial)	164.960(17)	166.11(3)	171.162(12)	171.525(12)	171.3(5)
M–O	2.502(6)	2.528(11)	2.484(8)	2.515(6)	2.52(2)

^a The distances are given as average values.

many new Pu(IV) complexes containing ligands suitable for studies that deeply probe covalency and electronic structure.

Conclusion

We have reported six new crystal structures of molecular Pu complexes. The metrical data presented here expands upon existing knowledge of the reactivity, structural, and bonding preferences in molecular Pu complexes and provides comparison with related f-metal ion complexes (Table 8). Such information can help development and lend validity to theoretical bonding descriptions of the transuranium elements, which are of great value given the relative difficulty in performing “hands-on” experiments with high-specific activity radioisotopes.

PuBr₃(thf)₄ (**1**) and Pu[N(SiMe₃)₂]₃Cl (**6**) offer new routes into non-aqueous/organometallic Pu(III) and Pu(IV) chemistry, respectively. The unexpected isolation of [PuI₂(thf)₄(py)][I₃] (**4**) and [PuCl₂(thf)₅][PuCl₅(thf)] (**5**) dem-

onstrate the apparent difficulty of isolating higher oxidation states of Pu in non-aqueous environments. In the systems we studied, a propensity to form (or remain unchanged as) Pu(III) ions was observed, which is surprising given the ease of formation and stability of Pu(IV) ions in aqueous solutions. Future studies will focus on utilizing **1** and **6** to explore the coordination chemistry, covalent bonding, and reactivity of Pu(III) and Pu(IV) ions in organic solvents under inert atmospheric conditions. We will also attempt to understand the apparent preference for Pu to autoionize relative to U and identify experimental conditions to prevent those pathways to facilitate facile syntheses of the target molecules we wish to study.

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Supporting Information Available: CIF's for **1–6**, NMR and electronic absorption spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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