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Structural Characterization of Pu[N(SiMe$_3$)$_2$]$_3$, a Synthetically Useful Nonaqueous Plutonium(III) Precursor

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A rare, and synthetically versatile, nonaqueous plutonium complex, Pu[N(SiMe$_3$)$_2$]$_3$ (**1**), has been structurally characterized by single-crystal X-ray diffraction for the first time and reveals significantly shorter agostic interactions compared to the cerium(III) analogue, indicating possible covalency differences.

Plutonium is a fascinating element with five accessible oxidation states (III−VII) in aqueous solutions, offering rich coordination possibilities and unique chemistry.[1] However, largely as a result of the high-specific radioactivity of available isotopes of plutonium, there is a paucity of structural and bonding information for molecular plutonium complexes. Interest in transuranic coordination chemistry is driven not only by scientific curiosity to understand the fundamentals of all of the accessible elements in the periodic table but also through a recognition that a comprehensive grasp of the basic electronic structure, bonding, and reactivity of the early to middle actinides (Th−Cm) is vital to support the development of advanced nuclear fuel cycles, and novel separation and waste remediation processes that are crucial to allow nuclear power to continue to play a significant role in meeting global energy demands.[2]

Specifically, the syntheses and characterization of molecular transuranic complexes in nonaqueous solvents are very limited. In the Cambridge Structural Database,[3] there are only a handful of entries of complexes that were prepared in the absence of water and oxygen. In contrast, the area of nonaqueous uranium coordination chemistry has flourished in the last few decades, yielding many surprising results that challenged contemporary views of the bonding, electronic structure, and reactivity possibilities in uranium molecular chemistry.[4] A similar evolution has not yet happened for the transuranic ions, and our current understanding of the electronic structure and bonding interactions of these elements stems almost entirely from aqueous systems for which the choice of ligands are limited to water-stable “hard” donors that will compete effectively to displace water/hydroxy ligands and coordinate to the metal center.[1,5] As a result, the bonding in those systems is predominately ionic. The extent to which covalency is important and the ability of the 5f and 6d valence electrons to participate in bonding have not been established beyond uranium (i.e., the question “How does the actinide contraction impact the electronic and bonding interactions of the metal ions across the 5f series?” has received scant experimental examination). Moving into nonaqueous solvents under inert atmospheric conditions allows access to a wider variety of ligands and donor atoms to probe and “tune” covalent interactions. The only fully structurally characterized molecular plutonium complexes with “soft” donors that we are aware of are Pu(9-aneS$_3$)I$_3$(CH$_3$CN)$_2$ (9-aneS$_3$ = 1,4,7-trithiacyclononane),[6] Pu(tpza)I$_3$(CH$_3$CN) (tpza = tris[(2-pyrazinyl)methyl]amine),[6] Pu(CH$_3$CN)$_9$[PF$_6$]$_3$,[7] and Pu(Et$_2$NCS$_2$)$_4$.[8] We are attempting to explore this immature field by preparing nonaqueous plutonium complexes with ligand sets chosen to invoke some degree of covalency in the bonding. To be able to achieve this aim, a set of suitable and well-characterized precursors that are soluble in organic solvents are required. For plutonium(III), the only molecular nonaqueous starting materials that have

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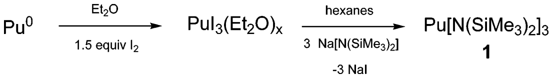
Scheme 1. Synthetic Route to **1**



$$Pu^0 \xrightarrow[\text{1.5 equiv } I_2]{Et_2O} PuI_3(Et_2O)_x \xrightarrow[\substack{3\ Na[N(SiMe_3)_2] \\ -3\ NaI}]{\text{hexanes}} \underset{\mathbf{1}}{Pu[N(SiMe_3)_2]_3}$$

been reported are $PuI_3(THF)_4$, $PuI_3(py)_4$, and $Pu[N(SiMe_3)_2]_3$ (**1**), none of which were characterized by single-crystal X-ray diffraction.[9] In that report, plutonium metal was oxidized by iodine in THF to isolate $PuI_3(THF)_4$ followed by treatment with $Na[N(SiMe_3)_2]$ to synthesize **1**. In our preliminary experiments, we found that careful control of iodine addition was required to avoid the undesired formation of $[PuI_2(THF)_5][I_3]$ during the synthesis of $PuI_3(THF)_4$. This led us to consider other routes to the silylamide without isolating $PuI_3(THF)_4$ first. In this manuscript, we present a modified synthesis and single-crystal structural determination of **1**.[10,11]

α-phase plutonium metal pieces were oxidized by iodine in diethyl ether. The resulting product was metathesized with $Na[N(SiMe_3)_2]$, and **1** was isolated from hexanes in 87% yield (Scheme 1). X-ray diffraction analysis was performed on a single-crystal obtained from an *n*-pentane solution of **1** stored at −30 °C.[12]

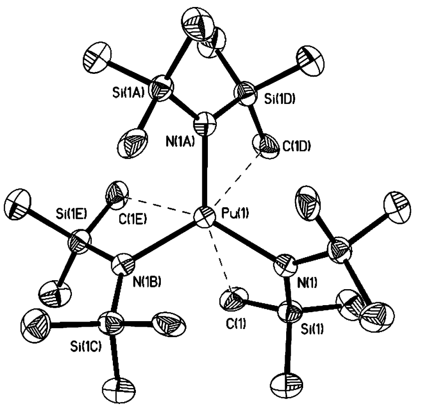


Figure 1. Thermal ellipsoid plot (50% probability level) of the structure of **1**·*n*-pentane (see also Table 1). The H atoms and lattice solvent have been omitted for clarity. The dashed lines represent the agostic interactions between the Pu atom and the methyl groups of the silylamide anions. Selected bond distance (Å) and angle (deg): Pu(1)−N(1) 2.315(10), N(1)−Pu(1)−N(1A) 113.97(5).

Table 1. Selected Crystallographic Data for **1**·*n*-Pentane

empirical formula	$C_{23}H_{66}N_3PuSi_6$
fw	792.31
space group	$P\bar{3}1c$
a (Å)	16.404(5)
b (Å)	16.404(5)
c (Å)	8.306(5)
α (deg)	90.00
β (deg)	90.00
γ (deg)	120.00
V (Å^3)	1935.7(13)
Z	2
D_{calc} (g cm^{-3})	1.365
μ (mm^{-1})	1.904
R1	0.0705
wR2	0.1628

The X-ray crystal structure of **1** reveals it to be comprised of a Pu atom coordinated to the three N atoms of the silylamide groups in a pyramidal geometry (Figure 1). The compound is isostructural with $U[N(SiMe_3)_2]_3$.[13] The Pu−N distance is 2.315(10) Å and is comparable with the reported U−N distance of 2.320(4) Å. The N−Pu−N angle is 113.97(5)° compared to the reported N−U−N angle of 116.24(7)°. The Pu atom lies 0.579 Å above the plane defined by the three N atoms of the silylamide groups, compared with 0.456(1) Å in the uranium complex. In the structure of **1**, there are agostic interactions between one of the methyl groups of each of the three silylamide anions and the Pu atom with a Pu(1)−C(1) distance of 2.968(9) Å. The N(1)−Si(1)−C(1) angle is 108.3(4)° and the Pu(1)−N(1)−Si(1) angle is 105.9(2)°, consistent with the direction of C(1) toward the Pu atom. All of the other C atoms are at distances of over 3.7 Å away from the Pu atom.

An interesting comparison to **1** is with the isostructural cerium(III) analogue.[14] Cerium(III) and plutonium(III) have very similar ionic radii (1.01 Å for cerium and 1.00 Å for plutonium, for a coordination number of 6),[15] and therefore any differences in M−N bond distances might be inferred as an indication of covalency differences between the

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(10) ***Safety note!*** Plutonium of weapons-grade isotopic composition was used in this research. The work was conducted in a radiological facility approved to contain high specific activity, α-particle-emitting radionuclides, with appropriate analyses of hazards and implementation of controls for the safe handling and manipulation of radioactive materials.

(11) Synthesis of $Pu[N(SiMe_3)_2]_3$ (**1**): Inside a negative-pressure helium-atmosphere drybox, α-phase plutonium metal (0.0257 g, 0.107 mmol) was suspended in Et_2O (5 cm^3) and iodine (0.0382 g, 0.151 mmol) added. The mixture was stirred at room temperature for 2 days, resulting in a very pale-blue powder, a small piece of unreacted plutonium metal (<2 mg), and a colorless solution, which indicated quantitative iodine consumption. $Na[N(SiMe_3)_2]$ (0.0552 g, 0.301 mmol) in Et_2O (2 cm^3) was added and stirred for 45 min to give an orange solution with a white precipitate of NaI. The solution was filtered, the solvent removed in vacuo from the filtrate, and the residue dissolved in hexanes (5 cm^3). The resultant orange solution was filtered and the solvent removed in vacuo to give an orange powder (0.0628 g, 87% yield based on iodine). Identification of the orange powder as **1** was made by comparison to the reported ^{1}H NMR and electronic absorption spectroscopic data.[9] Single-crystals suitable for X-ray diffraction were grown from a concentrated *n*-pentane solution of **1** stored at −30 °C for several days.

(12) Crystallographic data collection details: The crystal was coated with Paratone N and mounted inside a 0.5 mm capillary, which was sealed with wax and whose external surface was 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 were collected on a Bruker SMART APEX II CCD X-ray diffractometer with a KRYOFLEX liquid-nitrogen vapor cooling device at 141(2) K. The instrument was equipped with a Mo Kα X-ray source (λ = 0.710 73 Å), with MonoCap X-ray source optics. A hemisphere of data was collected using ω scans, with 5 s frame exposures at 0.3° frame widths. Data collection and initial indexing and cell refinement were handled with *APEX II* software.[18] Frame integration, including Lorentz−polarization corrections and final cell parameter calculations, was carried out using SAINT+ software.[19] The data were corrected for absorption with the *SADABS* program.[20] Decay of the reflection intensity was monitored via analysis of redundant frames. The structure was solved using direct methods and difference Fourier techniques. All H atom positions were idealized, and all H atoms rode on the atom that they were attached to. All non-H atoms were refined anisotropically. Structure solution, refinement, graphics, and creation of publication material were performed using *SHELXTL*.[21] The molecule was disordered on a site of 32 (D_3) symmetry. The 32 axis lies at the midpoint between two disordered Pu positions. The N atom positions occupy sites of two-fold rotation symmetry. The Pu atom positions were refined at half-occupancy. Two disordered pentane molecules per unit cell were treated using PLATON/SQUEEZE. This treatment corresponded to a solvent void space of 404.2 Å^3 and 64 electrons per unit cell.

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bonding in analogous Ln(III) and An(III) complexes. In $Ce[N(SiMe_3)_2]_3$, the Ce atom lies 0.310 Å above the plane defined by the three N atoms and the Ce−N distance is 2.320(3) Å, not statistically different from the Pu−N distance of 2.315(10) Å in **1**. However, the agostic interactions in $Ce[N(SiMe_3)_2]_3$ have a Ce−C distance of 3.106 Å, which is longer by 0.138 Å than the corresponding Pu−C distance in **1**. A recent report by Roger et al. noted a stronger agostic interaction in uranium arylthiolate complexes relative to the lanthanide analogues, evidenced by shorter U−C distances compared to Ln−C distances.[16] These results can be interpreted as an indication of the An(III) ions displaying a modest enhancement in covalency over the Ln(III) ions of similar ionic radii. Establishing the nature of these bonding differences with “soft” donors has implications of particular importance in the understanding and development of industrial trivalent An/Ln separations.

$U[N(SiMe_3)_2]_3$ has found great utility in advancing our understanding of uranium(III) chemistry, and we fully expect **1** to serve the same purpose for plutonium chemistry. We are currently using **1** as a precursor to explore a wide variety of nonaqueous and organometallic plutonium(III) complexes. Reactions with protonated imidodiphosphinochalcogenide ligands[17] suggest that **1** provides an effective entry route into unchartered areas of plutonium molecular chemistry.

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Note Added after ASAP Publication. This paper was released ASAP on October 11, 2007 with the wrong formula in reference to footnote 9. The correct version was posted on October 12, 2007.

Supporting Information Available: X-ray crystallographic data in CIF format for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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