

Preparation and structures of homoleptic Pu(III) and U(III) acetonitrile salts

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Nine-coordinate homoleptic acetonitrile solvate complexes of Pu(III) and U(III) ions have been prepared through oxidation of Pu metal suspended in acetonitrile with metal-hexafluorophosphate salts and dissolution of $U_3(THF)_4$ in acetonitrile, respectively.

We are studying low-valent actinide (U–Cm) complexes with the goals of understanding fundamental An(III) coordination chemistry and developing new agents for selective separations. These efforts require starting materials with varying properties, leading us to investigate alternatives to the oxidation of metals by iodine.^{1–3} We report here the preparation of the first homoleptic acetonitrile actinide complexes, $[Pu(NCMe)_9][PF_6]_3 \cdot MeCN$ (**1**), and $[U(NCMe)_9][I]_3$ (**2**).

Complex **1** is prepared by treating an acetonitrile suspension of ^{239}Pu metal turnings under argon atmosphere with three equivalents of either $AgPF_6$ or $TiPF_6$. The acetonitrile solution gradually turns blue as Pu metal dissolves and silver or thallium metal precipitates. Filtration of the solution followed by slow evaporation of acetonitrile results in the formation of blue crystalline $[Pu(NCMe)_9][PF_6]_3 \cdot MeCN$ in 80% isolated yield.⁴

Compound **1** is soluble in acetonitrile and insoluble in ether, tetrahydrofuran, hexanes, benzene, and dichloromethane. The crystal structure of **1**[†] shows a $[Pu(NCMe)_9]^{3+}$ cation (Figure 1) surrounded by three non-coordinating hexafluorophosphate anions. The central Pu atom is bound by nine acetonitrile nitrogen atoms to form a distorted tricapped trigonal prism. The six apical Pu–N distances range between 2.565 and 2.591 Å with an average Pu–N distance of 2.574 Å. The three capping Pu–N distances in **1** range between 2.554–2.573 Å with an average Pu–N distance of 2.572 Å. The most significant deviation of bond angles from ideal are 131° for N(7)–Pu(1)–N(1) and 103° for N(7)–Pu(1)–N(3). The dihedral angle between the N(8)–N(2)–N(5) and N(4)–N(6)–N(9) planes that define the top and bottom of the trigonal prism is 13°.

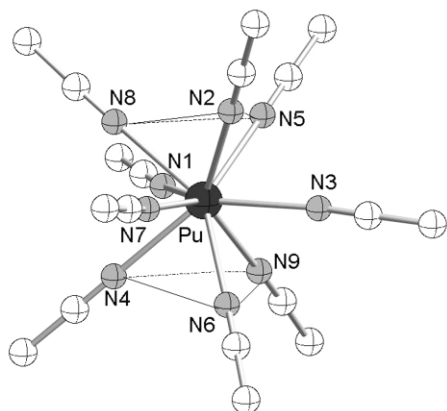


Fig. 1 Structure of the Pu(III) cation in **1**. Selected bond lengths (Å): Pu(1)–N(7) 2.554(4), Pu(1)–N(1) 2.561(4), Pu(1)–N(8) 2.565(4), Pu(1)–N(5) 2.566(4), Pu(1)–N(3) 2.573(4), Pu(1)–N(4) 2.575(5), Pu(1)–N(2) 2.579(5), Pu(1)–N(6) 2.582(4), Pu(1)–N(9) 2.591(4). Selected bond angles (°): N(7)–Pu(1)–N(1) 131.00(14), N(1)–Pu(1)–N(3) 126.37(13), N(7)–Pu(1)–N(3) 102.62(14).

Useful comparisons can be made between **1** and the structurally similar nine-coordinate Pu(III) aquo complex $[Pu(OH_2)_9][OTf]_3$ (**3**).⁵ The average Pu–O bond length in complex **3** (2.525 Å) is 0.047 Å shorter than the average Pu–N distance in complex **1** (2.572 Å). Diffuse reflectance spectra obtained on ground crystals of **1** and **3** are nearly superimposable, but each feature in the spectrum of **3** is blue-shifted by ~15 nm (83 eV) relative to that of **1**. As expected, structural and spectroscopic data reflect that the O atoms of water are slightly stronger sigma donors than the N atoms of acetonitrile towards the Pu(III) center.

Attempts to isolate the uranium analogue of **1** by treatment of oxide-free uranium turnings suspended in acetonitrile with either $AgPF_6$ or $TiPF_6$ were unsuccessful.⁶ However, dissolution of $U_3(THF)_4$ in acetonitrile followed by cooling to -35 °C yields dark green crystals of the target homoleptic U(III) acetonitrile complex $[U(NCMe)_9][I]_3$ (**2**).⁷ The crystals of **2**, unlike the Pu analogue **1**, are thermally unstable and rapidly decompose at room temperature to yield an intractable black residue.⁸ The 1H NMR spectrum of $U_3(THF)_4$ dissolved in CD_3CN shows two paramagnetically shifted resonances for the α and β hydrogens of free THF⁹ and implies formation of $[U(NCCD_3)_9][I]_3$ in solution.

Figure 2 show the cation of **2**. In contrast to the plutonium complex **1**, the uranium acetonitrile adduct **2**[‡] displays almost idealized tricapped trigonal prismatic geometry. The six prismatic U–N distances are 2.60 Å. The difference between the average prismatic M–N distances of **1** and **2** is 0.026 Å which is close to the 0.025 Å difference in the atomic radii of U and Pu.¹⁰ The three 2.65 Å capping U–N interactions in **2** are longer than the prismatic interactions by 0.05 Å, and 0.087 Å longer than the average Pu–N capping interactions in **1**. This U–N capping distance is 0.062 Å longer than that predicted by atomic radii differences between U(III) and Pu(III).

The actinide structures herein can be compared to the reported nine-coordinate acetonitrile lanthanide(III) tricapped

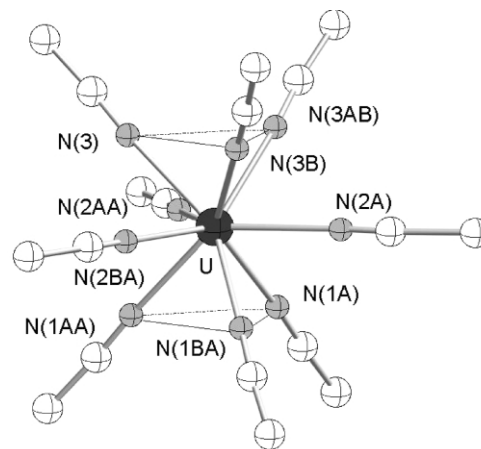


Fig. 2 Structure of the U(III) ion in **2**. Selected bond lengths (Å): U(1)–N(1) 2.60(2), U(1)–N(2) 2.65(2), U(1)–N(3) 2.60(2). Selected bond angles (°): N(2BA)–U(1)–N(2A) = N(2BA)–U(1)–N(2AA) = N(2AA)–U(1)–N(2A) = 120°.

trigonal prismatic adducts, $[\text{Ln}(\text{NCMe})_9][\text{X}]_3$ ($\text{Ln} = \text{La}, \text{Sm}; \text{X} = \text{AsF}_6^-$ and $\text{Ln} = \text{Pr}; \text{X} = \text{AlCl}_4^-$).¹¹ The three capping Ln-distances are on average slightly shorter than the six prismatic ones in the crystal structures of La ($\Delta_{\text{avg}} = 0.016 \text{ \AA}$) and Pr ($\Delta_{\text{avg}} = 0.004 \text{ \AA}$). This trend reverses in the Sm complex ($\Delta_{\text{avg}} = 0.008 \text{ \AA}$). However, the difference between the average prismatic and average capping distance in a particular $\text{Ln}(\text{NCMe})_9^{3+}$ compound is small. The DFT calculations performed on the nine-coordinate acetonitrile Ln^{3+} ($\text{Ln} = \text{Eu}, \text{Yb},$ and La) solvates predicted that the three capping distances of $\text{Ln}(\text{NCMe})_9^{3+}$ would be longer than the six prismatic distances.¹² Qualitatively, uranium complex **2** follows the trend predicted by DFT, but the plutonium complex **1** follows the trend of the experimentally determined Ln structures.

A variety of U(III) compounds related to acetonitrile complexes **1** and **2** have been prepared from UI_3 ,¹³ $\text{UI}_3(\text{THF})_4$,¹⁴ and $\text{UI}_3(\text{py})_4$.^{15–17} These compounds contain nitrogen donor ligands and serve as structural models for developing extractants for nuclear fuels reprocessing. These studies reveal that iodide can be displaced from a UI_3 coordination sphere by multidentate N-donor ligands, as evidenced by the reaction between $\text{UI}_3(\text{py})_4$ and 2,2':6',2''-terpyridine (terpy).¹⁵ When two equivalents of terpy in pyridine are added to a pyridine solution of $\text{UI}_3(\text{py})_4$, the bis terpy complex $[\text{UI}_2(\text{terpy})_2(\text{py})]\text{I}$ (**4**) is isolated. Complex **4** is stable in pyridine in the presence of excess terpy and no exchange is observed between the free and coordinated ligand. In contrast, treatment of $\text{UI}_3(\text{py})_4$ with three equivalents of terpy in acetonitrile generates $[\text{U}(\text{terpy})_3]\text{I}_3$ (**5**). Complex **5** can be transformed into **4** with liberation of a terpy molecule upon dissolution in pyridine. Isolation of **2** by dissolution of $\text{UI}_3(\text{THF})_4$ in acetonitrile, however, implies that acetonitrile present in large excess can displace either thf or iodide coordinated to U(III) and that multidenticity is not required for an inner sphere iodide to be displaced. Therefore complex **2** is likely present along the reaction pathway towards the formation of **5**.

In conclusion, complexes **1** and **2** are the first structurally characterized homoleptic actinide nitrile adducts. Reaction of plutonium metal with silver and thallium hexafluorophosphate salts in acetonitrile cleanly provides the Pu(III) acetonitrile salt **1** in high yield. Complex **1** represents the first homoleptic molecule containing a nine-coordinate anhydrous plutonium (III) ion. Homoleptic acetonitrile uranium (III) complex **4** is accessed by dissolution of $\text{UI}_3(\text{THF})_4$ in acetonitrile. These results underscore the limited complexing ability of iodide towards U(III) even in the absence of sterically bulky multidentate nitrogen donor ligands. Understanding the differences in reactivities of uranium and plutonium with oxidants in non-aqueous media remains a key part of our efforts to prepare low-valent actinide complexes relevant to extraction processes.

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Notes and references

† Crystal data for **1**: $\text{C}_{20}\text{H}_{27}\text{F}_{18}\text{N}_{10}\text{P}_3\text{Pu}$, $M = 1084.43$, $a = 11.9803(6)$, $b = 12.9930(6)$, $c = 13.3702(7) \text{ \AA}$, $\alpha = 92.0600(10)$, $\beta = 96.4600(10)$, $\gamma = 103.4470(10)^\circ$, $V = 2007.14(17) \text{ \AA}^3$, triclinic space group $P1$, $Z = 2$, $T = 203 \text{ K}$, $R1(I > 2\sigma) = 0.0342$, and $wR2(I > 2\sigma) = 0.0726$. All crystal data were collected on a Bruker P4/CCD using ϕ scans. The structures for both **1** and **2** were solved using standard direct methods techniques on F^2 (SHELXS-97), and refined using full-matrix least-squares based on F^2 (SHELXL-97). Hydrogen atom positions were idealized and all non-hydrogen atoms were refined anisotropically. Two of the PF_6^- anions in **1**

were modeled for disorder by refining two overlapping octahedra with a central pivot point; the disorder refined to 60% and 40% for the major and minor components respectively. CCDC 207441. See <http://www.rsc.org/suppdata/cc/b3/b303558a/> for crystallographic data in .cif or other electronic format.

‡ Crystal data for **2**: $\text{C}_{18}\text{H}_{27}\text{I}_3\text{N}_6\text{U}$, $M = 988.22$, $a = 10.974(4)$, $c = 24.475(11) \text{ \AA}$, $V = 2552.7(9) \text{ \AA}^3$, trigonal space group $R\bar{3}$, $Z = 3$, $T = 203 \text{ K}$, $R1(I > 2\sigma) = 0.0737$, and $wR2(I > 2\sigma) = 0.1273$. (Refinement in $R\bar{3}m$ resulted in $R1 = 0.12$.) The $[\text{U}(\text{NCCH}_3)_9][\text{I}]_3$ molecule is disordered on a site of 3 bar crystallographic symmetry. Thus, each acetonitrile group occupies a general position of $\frac{1}{3}$ -occupancy. CCDC 207442. See <http://www.rsc.org/suppdata/cc/b3/b303558a/> for crystallographic data in .cif or other electronic format.

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- Finely divided Pu metal turnings (0.100 g, 0.4 mmol) were treated with 2 mL of acetonitrile and 0.25 g (1.0 mmol) of AgPF_6 . Formation of a blue solution is observed within 30 min. The mixture was stirred for 24 h and the supernatant solution was filtered using a syringe filter. The filtered solution was allowed to slowly evaporate in the drybox to give a single large blue-green crystal weighing 0.243 g (80% yield based on $\text{Pu}(\text{MeCN})_9(\text{PF}_6)_3 \cdot \text{MeCN}$).
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- A green solution formed within 5 hours when U metal turnings were suspended in acetonitrile and treated with AgPF_6 . A small amount of a viscous green residue was obtained after evaporation of acetonitrile, but no crystalline material could be isolated. No reaction between U metal and TIPF_6 was observed after 72 hours. A similar reaction using $\text{TIBAr}_4^{\text{F}}$ ($\text{BAr}_4^{\text{F}} = \text{tetrakis}(3,5\text{-bis}(\text{trifluoromethylphenyl})\text{borate})$) as the oxidant showed no reaction after 1 month.
- An Erlenmeyer flask was charged with 1.052 g of $\text{UI}_3(\text{THF})_4$ and 25 mL of acetonitrile. This green solution was stirred for 30 minutes then filtered through a celite padded coarse fritted filter. The dark-green filtrate was placed into a -35°C freezer for 24 h and large green crystals formed. These crystals dissolve into the acetonitrile if the supernatant is allowed to reach room temperature. Rapid transfer of the crystals to a drop of Paratone-N followed by cooling of the container in a liquid nitrogen cooled sand-bath allowed for X-ray diffraction analysis without decomposition.
- Dissolution of this residue into acetonitrile followed by cooling to -35°C reforms dark green crystals of **2**. Unfortunately, the extreme thermal instability of **2** did not allow us to obtain elemental analysis, or additional analytical data.
- The chemical shifts of these resonances depend on the concentration of the paramagnetic U(III) species and the sample solution temperature. The 300 MHz ^1H NMR spectrum of a 50 mM $\text{UI}_3(\text{THF})_4$ in CD_3CN displays two THF resonances at $\delta = 4.40$ ppm and $\delta = 2.46$ ppm relative to residual CHD_2CN . Cooling the sample to -30°C results in a slight downfield shift of the resonances to $\delta = 4.72$ and $\delta = 2.86$ ppm. An identical NMR sample spiked with a drop of THF displays similar behaviour except that the THF resonances are narrower. At room temperature the THF-spiked sample shows resonances at $\delta = 4.38$ and $\delta = 2.45$ ppm. These resonances shift to 4.52 and 2.61 ppm as the sample is cooled to -30°C . These data suggest that THF is not exchanging into the inner sphere of the complex on the NMR timescale and that the hydrogen signals for free THF are paramagnetically shifted by $\text{U}(\text{NCCD}_3)_9\text{I}_3$ present in solution.
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