An entry route into non-aqueous plutonyl coordination chemistry†

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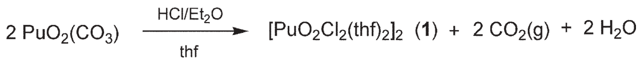
The Pu(VI) molecular complex, $[PuO_2Cl_2(thf)_2]_2$, is prepared by addition of a HCl/Et$_2$O solution to a suspension of PuO_2CO_3 in thf, yielding the first example of a precursor suitable for investigation of the non-aqueous chemistry of the plutonyl dioxo cation under inert atmospheric conditions.

Hexa- and penta-valent 5f ions (U, Np, Pu and Am) exist predominately as the actinyl AnO_2^{2+} and AnO_2^{+} dioxo species, respectively. The best studied of these ions is uranyl, UO_2^{2+}, whose chemistry in aqueous solutions with 'hard' oxygen donor ligands has been widely investigated.[1] Non-aqueous uranyl complexes have been researched far less intensively, yet are crucial to fully understanding the bonding and electronic properties of actinyl ions.[2] A striking example of the effect the co-ligands can have on actinyl behavior is the use of electron-rich ligands in the equatorial plane of uranyl to increase the Lewis basicity of the uranyl oxo oxygen atoms, resulting in direct coordination to a Lewis acid.[2a]

As the chemistry of the uranyl ion is advanced, fundamentally important questions arise: (1) What is the effect of the actinide contraction on the chemistry of the actinyl ions as they become progressively 'harder' and more ionic across the 5f series? (2) Are there significant consequences of 5f orbital occupation across the series ($5f^0$, $[UO_2]^{2+}$; $5f^1$, $[NpO_2]^{2+}$; $5f^2$, $[PuO_2]^{2+}$; $5f^3$, $[AmO_2]^{2+}$) and how do they affect the structural and bonding properties of the actinyl ions? Answering these questions, however, is synthetically very challenging because of the high specific α-activity of available Np, Pu and Am radionuclides and the relative instability of the +VI oxidation state compared to uranium.‡ Indeed, only four molecular PuO_2^{2+} complexes (three of which were prepared hydrothermally) have been characterised by single-crystal X-ray diffraction[3] and as a result, even under aqueous conditions, there is only a relatively primitive understanding of the chemistry of the PuO_2^{2+} cation. Progression of plutonyl coordination chemistry to non-aqueous systems has not been reported, yet is a necessity for fully developing an understanding of the structure and bonding interactions of transuranic actinyl ions and their complexes.

Here we report the synthesis of $[PuO_2Cl_2(thf)_2]_2$ **1**, which is the first complex to allow investigation of the plutonyl ion in non-aqueous environments.§ Dissolution of a thf suspension of plutonyl carbonate powder[4] (PuO_2CO_3) by addition of a slight excess of 1.0 M HCl in Et$_2$O results in the formation of a yellow–orange solution. After removal of volatiles, the residue was taken up in thf and excess TMSCl (chlorotrimethylsilane) was added to remove any residual water present in the system. Addition of hexanes affords **1** as an orange–yellow powder in 83% yield (Scheme 1). X-Ray diffraction quality crystals of **1** were obtained by vapor diffusion of *n*-pentane into a thf solution of **1** at ambient temperature.¶ Complex **1** is soluble in thf, acetonitrile, DME and pyridine but is insoluble in toluene, dichloromethane, *n*-pentane, hexanes and diethyl ether.



$$2\,PuO_2(CO_3) \xrightarrow[\text{thf}]{\text{HCl/Et}_2\text{O}} [PuO_2Cl_2(thf)_2]_2\ (\mathbf{1}) + 2\,CO_2(g) + 2\,H_2O$$

Scheme 1 Preparative route for synthesis of **1**.

The solid-state molecular structure of **1** (Fig. 1) consists of a dimer, which lies about an inversion centre, of plutonyl cations bridged by two chloride anions. For each plutonium atom a terminal chloride anion and two oxygen atoms of coordinated thf molecules complete the slightly distorted pentagonal bipyramidal geometry around the Pu centre. The axial Pu–O distances are 1.725(9) and 1.714(9) Å, while the O(1)–Pu(1)–O(2) angle is 179.5(5)°, consistent with a linear PuO_2^{2+} ion. The bridging Pu–Cl distances are 2.810(4) and 2.800(4) Å, and the terminal Pu–Cl distance is 2.645(4) Å. The coordinated thf molecules have Pu–O bond lengths of 2.397(9) and 2.401(10) Å. The Pu–O axial distances are similar to those in $[PuO_2\{(OOC)_2C_6H_4\}H_2O]\cdot H_2O$ (1.727(4) and 1.731(4) Å).[3c] Complex **1** is isostructural, but not isomorphous, with $[UO_2Cl_2(thf)_2]_2$,[5] the most widely used synthon in non-aqueous uranyl chemistry. The Pu–O axial and Pu–Cl bond distances would be expected to be slightly shorter in **1** than in the $[UO_2Cl_2(thf)_2]_2$ due to the higher *z*/*r* of Pu(VI) compared to U(VI). Unfortunately, the errors associated with the metrical parameters of $[UO_2Cl_2(thf)_2]_2$ are too large to determine if they are statistically

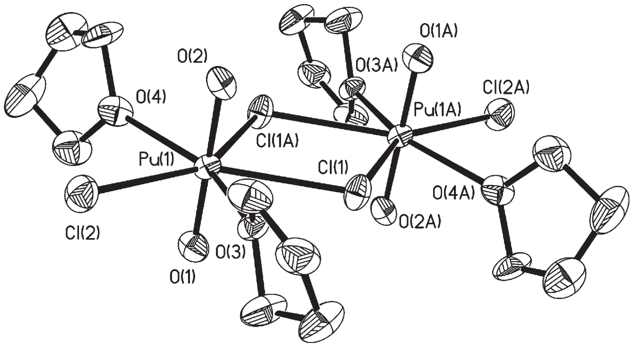


Fig. 1 Thermal ellipsoid plot (50% probability level) of the structure of **1**; H atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Pu(1)–O(1) 1.714(9), Pu(1)–O(2) 1.725(9), Pu(1)–Cl(1) 2.810(4), Pu(1)–Cl(1A) 2.800(4), Pu(1)–Cl(2) 2.645(4), Pu(1)–O(3) 2.397(9), Pu(1)–O(4) 2.401(10); O(1)–Pu(1)–O(2) 179.5(5). The letter A denotes atoms at equivalent positions (−*x*, 2 − *y*, −*z*).

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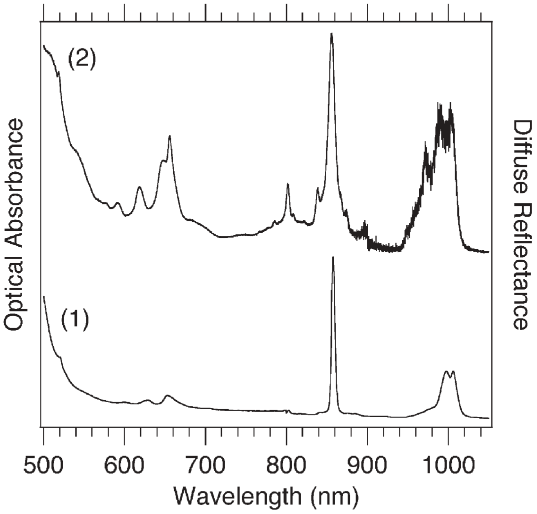

Fig. 2 Electronic absorption spectrum of **1** in thf solution (1) and diffuse reflectance of solid **1** (2).

different than those of **1**; the U–O axial distances are 1.76(3) and 1.74(2) Å, the terminal U–Cl distances are 2.66(3) and 2.65(2) Å, while the bridging U–Cl distances are 2.80(2), 2.81(2), 2.83(2) and 2.32(2) Å.

The solution UV/vis/nIR spectrum of **1** in thf (Fig. 2) exhibits a prominent absorbance band at 858 nm, due to a 5f–5f transition in the PuO_2^{2+} moiety, a significant shift from the corresponding band of the aquo complex in 1 M $HClO_4$, which occurs at 830 nm.[6] The transition in **1** at 858 nm can also be compared to plutonyl chloride complexes formed in aqueous solution by addition of NaCl to a 0.1 M $HClO_4$ solution of Pu(VI),[7] in which electronic transitions at 838 and 843 nm have been attributed to PuO_2Cl^+ and PuO_2Cl_2 complexes, respectively. The diffuse reflectance UV/vis/nIR spectrum of **1** as a solid (Fig. 2) has an absorbance at 856 nm and compares well with the thf solution spectrum of **1**, suggesting the speciation is similar in thf solution as in the solid phase.

The ^1H NMR spectrum of **1** in thf-d_8 displays resonances for coordinated and uncoordinated thf molecules, and there are no other significant peaks in the spectrum. The ^{31}P NMR spectrum of **1** in thf-d_8, after addition of 4 equiv. of TPPO (triphenylphosphine oxide) (Pu : TPPO ratio of 1 : 2) displays a major broad, paramagnetically shifted, resonance at -146 ppm, which we attribute to the formation of a 1 : 2 PuO_2^{2+} complex with TPPO ($PuO_2Cl_2(TPPO)_2$). A smaller resonance is observed (of about 8 times less intensity) at -16 ppm, which is likely due to a 1 : 1 Pu : TPPO complex and not free TPPO. Employing a Pu : TPPO ratio of 1 : 10, the ^{31}P NMR spectrum has a resonance at 25 ppm for free TPPO and a resonance at -144 ppm for the 1 : 2 complex but no observable signal for a 1 : 1 complex at -16 ppm (although due to the paramagnetism of Pu(VI), the moderate solubility of the complexes and the long NMR acquisition times that are required, a small amount of 1 : 1 complex may still be present). At Pu : TPPO ratios of 1 : 0.5 and 1 : 1 only a resonance at -16 ppm for the 1 : 1 complex is observed.

As the ratio of Pu : TPPO increases from 1 : 0.5 to 1 : 10 the electronic transition, in the UV/vis/nIR spectra, for **1** at 856 nm decreases in intensity along with the emergence of a new peak at 879 nm. Given the fact that the ^{31}P NMR spectra indicates the presence of both 1 : 1 and 1 : 2 complexes in solution it is not clear why only one new transition is observed in the UV/vis/nIR spectra instead of two new transitions. A possible explanation is that the peak at 879 nm is due to the 1 : 1 complex and that no transition is observed for the 1 : 2 complex because if the 1 : 2 complex has an expected *trans* geometry then it is centrosymmetric and the electronic transition is forbidden. This phenomenon has been reported in the literature for centrosymmetric solid-state Np(V) complexes,[8] for which there were no absorbances in the 980 nm region, and was more recently noted for centrosymmetric Np(V) complexes in solution.[9] Whilst it is clear that the thf molecules in **1** are readily displaced by neutral donors such as TPPO to form new complexes, the data does not conclusively ascertain the speciation in solution. Although the primary intent of this communication is to present unprecedented synthetic access to a non-aqueous Pu(VI) precursor, these preliminary reactivity explorations with TPPO illustrate the future opportunities for extensive spectroscopic studies to provide insights into the electronic structure of the PuO_2^{2+} ion.

In acidic aqueous solutions, ^{239}Pu(VI) has been reported to reduce at a rate of approximately 1.5% per day to Pu(V), which then disproportionates to Pu(VI) and Pu(IV).[10] The mechanism of the reduction arises from reaction of Pu with the radiolysis products of water caused by the α-particle emission of ^{239}Pu. A precipitate begins to form after several hours to a few days from a thf solution of **1**, rendering it difficult to asses the stability of **1** in thf solution. However, complex **1** appears to have greater solubility in CH_3CN. The UV/vis/nIR spectrum of **1** in CH_3CN is slightly different than in thf suggesting a change in PuO_2^{2+} speciation, as evidenced by a shift in the band at 858 nm to 850 nm and the appearance of a shoulder at approximately 854 nm. Over a period of 7 days (kept in the dark to negate any possible photochemical redox processes), the UV/vis/nIR spectrum of **1** in CH_3CN showed a decrease in the intensity of the absorbance at 850 nm by approximately 10%. Despite this decrease, there was no observation of any new peaks emerging in the spectrum that would be expected if Pu(VI) was reduced to soluble molecular species containing lower valent plutonium, suggesting that the speciation in solution is not changing over time and the apparent 'loss' of Pu(VI) in solution is likely a result of some precipitation of plutonium. We do not know if the precipitated material contains Pu(VI), Pu(IV) or Pu(III).

In conclusion, we have established a facile entry into non-aqueous plutonyl chemistry by isolating $[PuO_2Cl_2(thf)_2]_2$, thus opening up the possibility to fully explore the bonding and electronic properties of the paramagnetic $5f^2$ $[PuO_2]^{2+}$ cation compared with the diamagnetic $5f^0$ $[UO_2]^{2+}$ cation and we are currently utilizing **1** to investigate the chemistry of the plutonyl(VI) ion in anhydrous and inert atmosphere environments. In this regard, complex **1** is a particularly attractive synthon as the thf ligands should be readily displaced by other Lewis bases, a proposal supported by our preliminary results and displacement of thf by TPPO, while the chloride ligands should easily undergo exchange *via* salt metathesis. We are conducting further experiments to explore the synthetic utility of **1** to prepare a range of non-aqueous plutonyl complexes. The potential importance of **1** is highlighted by its uranyl analogue, which has been, and remains, invaluable in the pursuit and realisation of hitherto unknown aspects of the electronic structure and reactivity of the UO_2^{2+} cation. A similar level of synthetic capability and advancement for the transuranic actinides must be also achieved before the chemical community can acquire a comprehensive understanding of the structure and bonding of the 5f actinyl ions.

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Notes and references

‡ *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-emitting radionuclides, with appropriate analyses of hazards and implementation of controls for the safe handling and manipulation of radioactive materials. Due to the stringent sample containment and safety requirements, which must be compliant with regulations, we could not acquire elemental analyses, IR or Raman spectra on air-sensitive plutonium compounds.

§ *Synthesis* of **1**: Inside a negative pressure helium atmosphere dry-box, PuO_2CO_3 (0.0583 g, 0.176 mmol) was suspended in thf (5 cm^3) and 1.0 M HCl in Et_2O (0.40 cm^3) added. The mixture was stirred for 40 min to give a slightly cloudy orange–yellow solution. The solvent was removed *in vacuo* and the yellow–orange residue dissolved in thf (7 cm^3) and 7–8 drops of TMSCl was added and the solution stirred for 15 min. Hexanes (12 cm^3) were added and the solution stirred for 10 min resulting in precipitation of an orange–yellow solid. The suspension was stored at −35 °C for 1 h, and then the almost colourless solution was pipetted away from the solid, which was then washed with hexanes (7 cm^3) and dried *in vacuo* to give an orange–yellow powder (0.0707 g, 83% yield). Single crystals suitable for X-ray diffraction were obtained by vapor diffusion of *n*-pentane into a concentrated thf solution of **1**.

^1H NMR (C_4D_8O): δ 1.75, 3.58 (s, free thf); 1.80, 3.62 (m, coordinated thf).

UV/vis/nIR: (in thf) (λ/nm (ε/M^{-1} cm^{-1})); 245 (4309), 292 (3669), 318 (3852), 408 (1539), 435 (1553), 629 (47), 653 (66), 858 (585), 998 (156), 1006 (156).

Diffuse reflectance UV/vis/nIR (λ/nm): 519, 591, 619, 647, 656, 786, 802, 809, 839, 856, 972, 989, 1004.

¶ *Crystal data* for **1**: $C_{16}H_{32}Cl_4O_8Pu_2$, M = 972.24, triclinic, space group $P\bar{1}$, a = 7.063(3), b = 9.720(3), c = 10.189(4) Å, α = 78.691(4), β = 79.847(4), γ = 81.777(3)°, V = 670.9(5) Å^3, T = 141(2) K, Z = 2, μ = 5.303 mm^{-1}, reflections collected/independent = 6571/2452 (R_{int}= 0.0698), R_1 ($I > 2\sigma(I)$) = 0.0543 and wR_2 ($I > 2\sigma(I)$) = 0.1038. CCDC 631420. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b618577k

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