Synthesis, characterization, and theoretical analysis of a plutonyl phosphine oxide complex

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The synthesis of trans-PuO₂Cl₂(OPcy₃)₂, 1-Pu, has been carried out and confirmed by single crystal X-ray diffraction along with UV-vis-NIR, and ³¹P NMR spectroscopies. Theoretical analysis finds that despite a higher calculated covalency for the Pu=Cl interaction, the Pu–OPcy₃ interaction is stronger due to the accumulation of electron density in the interatomic region. The coordination of equatorial ligands slightly decreases the strength of the PuO₂⁺ interactions relative to the free gas phase (PuO₂)²⁺ ion.

Phosphine oxides play a critical role in the recycling and separations of actinides e.g. the plutonium uranium reduction extraction (PUREX) process.¹ ² The structural and extraction behaviour of uranium-phosphine oxide compounds is well defined, in particular as the uranyl ion, (UO₂)²⁺.³ However, the structural chemistry of the transuranium actinyl compounds is far less developed with just a handful of Np⁶⁺/Pu⁶⁺ complexes that have been structurally characterized in the form AnO₂X₂(OPPh₃)₃, or [AnO₂(OPPh₃)]⁺X⁻ [X = Cl, NO₂; X' = ReO₄, ClO₄]₂.⁴⁻⁵ Recent examination of its saturated analogue, OPCI₃ (cy = cyclohexyl, C₆H₁₂) in mer-M¹¹¹Br₃(OPCI₃) (M = Am, La – Nd) showed an unusual amount of metal-based pseudo-core 5p/6p participation in bonding with the OPCI₃ ligand.¹⁰ The difference in saturation not only affects the steric profile of the molecules, but also the donation strength of the phosphine oxide via differing electronic structure.¹¹ The OPCI₃ ligand has been shown to be a stronger donor than OPPH₃ for actinyl ions, (An⁶⁺O²⁻)¹² (An = U, Np) but can be displaced by HNPCI₃ or HNPPH₃.⁵⁻⁷, ¹², ¹³ Although a synthesis of PuO₂Cl₂(OPcy₃)₂ has been reported as a conference proceeding that included a summary of the synthesis and the ³¹P NMR spectroscopy resonances, but not the solvent.¹³ Because of the uncertainty of the structural and in depth spectroscopic details of PuO₂Cl₂(OPcy₃)₂, we sought to re-examine it. Herein we continue the study of OPCI₃ with actinide complexes through structural, spectroscopic, and theoretical studies of trans-PuO₂Cl₂(OPcy₃)₂.

We began our investigation by revisiting and scaling down analogous uranyl chemistry using 15-20 mg of metal content, typical of plutonium chemistry. When a solution of OPRS (R = cy, Ph) was carefully layered on top of a solution of UO₂X₂•nH₂O in a polar solvent (EtOH for X = Cl; Acetone for X = NO₂), bright yellow X-ray quality crystals of trans-UO₂Cl₂(OPcy₃)₂, 1-U, trans-UO₂Cl₂(OPPh₃)₂, 2-U, trans-UO₂(NO₂)₂(OPcy₃)₂, 3-U, and trans-UO₂(NO₂)₂(OPPh₃)₂, 4-U, grew upon standing overnight, see ESI for synthetic details. While the structure of 1-U+DCM is known with a lattice DCM solvent molecule, synthesis in ethanol gave 1-U as the solvent free crystal structure featuring two crystallographically independent units, which both feature an inversion centre in the P1 space group. The bond metrics of 1-U compare well with 1-U+DCM,⁵ as well as with the OPPH₃ analogue, 2-U, see ESI for comparisons.¹⁴ ¹⁵ Complex 3-U is a new molecule and displays the anticipated 8-coordinate, distorted hexagonal bipyramidal geometry of similar complexes, such as the known OPPH₃ analogue 4-U.¹⁶

With this chemistry in hand, we extended our synthesis to plutonium, starting from freshly generated PuO₂Cl₂(H₂O)₆. A solution of PuO₂Cl₂(H₂O)₆ in methanol was carefully layered with a solution of OPCI₃ in ethanol, and upon slow evaporation of the solvent pale-yellow crystals of trans-PuO₂Cl₂(OPcy₃)₂, 1-Pu, formed. This was confirmed by single crystal X-ray crystallography, Fig. 1, eq. 1. 1-Pu was isolated in high yield following work up, and the sample was brought into a negative pressure glovebox dedicated to actinide chemistry. 1-Pu is isomorphous with 1-U crystallizing in the same P1¹ space group with two crystallographically independent units, each with one
Conversely, changes in $\delta(r)$ can also be considered as reference. In the QTAIM formalism, the chemical bond is understood by analyzing changes in the electron density, $\rho(r)$, as well as the delocalization index, $\delta(r)$, at the bond critical point (BCP). Increases in $\rho(r)$ are associated with increased covalency and results in a strengthening of the bond. This is accompanied by an increase in the $\delta(r)$, which is considered as an alternative bond-order descriptor. Conversely, changes in $\delta(r)$ can also be related to an increase in covalency without a change in the strength of the bond. The elucidation of the nature of the bond is further supported by the energy parameters derived from potential, $V(r)$, kinetic, $G(r)$, total $H(r)$, energy densities. Where $V(r)$ signifies a stabilization of electron density at the BCP, while $G(r)$ signifies destabilization due to an excess of kinetic energy at the BCP. Therefore, a negative $H(r)$ value corresponds to a quantification of covalent interactions. By normalizing the values, $H(r)/\rho(r)$, a “covalency degree” is obtained, and functions as a more general description of covalency.

For the sake of clarity, the discussion of the bonding in 1-U and 1-Pu will be addressed as a perturbation of the gas phase (AnO$_2$)$_{2+}$ ion. The interaction between An(VI) (An = U, Np, Pu) centres and oxo ligands has been widely studied, where Raman spectroscopy unequivocally suggests that the U=O$_x$ bonds are stronger than Pu=O$_x$.

To better understand the bonding in 1-Pu and 1-U, we turned to Complete Active Space Self Consistent Field (CASSCF) calculations to generate the corresponding molecular densities for analysis by Bader’s Quantum Theory of Atoms in Molecules (QTAIM). The active space consisted of $n$ electrons in 10 orbitals for the CAS ($n,10$) calculations on 1-Pu ($n = 8$) and 1-U ($n = 6$). To keep the structure imposed by the crystal packing, the coordinates from the crystal structure were used for the calculations without optimization, see ESI for further details. The corresponding gas phase (AnO$_2$)$_{2+}$ ions have been also considered as reference. In the QTAIM formalism, the chemical bond is understood by analysing changes in the electron density, $\rho(r)$, as well as the delocalization index, $\delta(r)$, at the bond critical point (BCP). Increases in $\rho(r)$ are associated with increased covalency and results in a strengthening of the bond. This is accompanied by an increase in the $\delta(r)$, which is considered as an alternative bond-order descriptor. Conversely, changes in $\delta(r)$ can also be related to an increase in covalency without a change in the strength of the bond. The elucidation of the nature of the bond is further supported by the energy parameters derived from potential, $V(r)$, kinetic, $G(r)$, total $H(r)$, energy densities. Where $V(r)$ signifies a stabilization of electron density at the BCP, while $G(r)$ signifies destabilization due to an excess of kinetic energy at the BCP. Therefore, a negative $H(r)$ value corresponds to a quantification of covalent interactions. By normalizing the values, $H(r)/\rho(r)$, a “covalency degree” is obtained, and functions as a more general description of covalency.

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According to the QTAIM metrics the coordination of the Cl$^{-}$ and OPcy$_3$ ligands in the equatorial plane weaken the An=O$_x$ bonds in both 1-U and 1-Pu, relative to (UO)$_2$ and (PuO)$_2$, respectively. This weakening is quantified as $\Delta$An=O$_x$, where the effect is more strongly observed in 1-U than in 1-Pu, Table S3. The perturbation of the An=O$_x$ bonds upon coordination of the Cl$^{-}$ is rather similar for both complexes, but the most significant weakening of the U=O$_x$ bonds is due to the coordination of the OPcy$_3$ ligands, given as $\Delta$An--L in Table S3. The weakening of the An=O$_x$ interaction is on the order of 12% and 6% [based on $\rho(r)$] for U and Pu, respectively. This weakening is shown by the significant reduction of the $\rho(r)$, $\delta(r)$, and $H(r)$ values at the U=O$_x$ BCP in 1-U relative to the (UO)$_2$ ion. Furthermore, the $\varepsilon(r)$ of 1-U deviates more significantly from zero than in 1-Pu, supporting the claim of weakening the U=O$_x$ interaction, Table S3.

As expected, the calculated bond covalency follows the charge of the ligand, O$^{2-}$ >> Cl$^{-}$ > OPcy$_3$, Table S3. It is important to note that despite the larger covalent character predicted for the An=Cl bonds (greater total energy densities), the An--OPcy$_3$ bonds are stronger (greater electron densities). This is also one
example showing that covalency does not necessarily correlate with bond strength.

To further understand these differences, Natural Localized Molecular Orbitals (NLMOs) have been calculated from the scalar relativistic CASSCF densities. NLMOs break down bonding interactions into the component orbitals, both from the bonding atoms, as well as the contributing orbital hybrids from each atom. Notably the NLMOs of the metal 6p, orbital display polarization of the semi-core electron density towards the 5f shell, where (PuO$_2$)$_2$\(^+\) > (UO$_2$)$_2$\(^+\), with 19% and 14% mixing, respectively, which is fundamental for the strengthening of the U=O$_2$ bonds in the so-called "Inverse Trans Influence" (ITI), Fig. S15.\(^{11}\) This polarization is reduced significantly upon the coordination of equatorial ligands to 6% (1-Pu), and 14% (1-U), suggesting that (UO$_2$)$_2$\(^+\) is more sensitive to ligand coordination, as also shown by the QTAIM metrics. The NLMO analysis also confirmed the An=O$_2$ interaction to be a triple bond consisting of one \(\sigma\)-type and two \(\pi\)-type bonds for all species, Fig. S15. Decomposition of the NLMOs indicates that the orbital hybrids are dominated by the 5f over the 6d orbitals. With (UO$_2$)$_2$\(^+\) again displaying increased sensitivity to ligand coordination over (PuO$_2$)$_2$\(^+\), as confirmed by: the occupation numbers, the contributions to the total bond order, and the hybrid overlaps, Fig. S15 & Table S4.

Examination of the bonding in the equatorial ligands suggests that the 6d orbitals dominate the NLMO compositions, with nearly equal contributions from 5f and 7s orbitals in the \(\sigma\)-based NLMOs. The better energy match between the actinide centre and the Cl–3p orbitals compared to O\(_2\)–2p orbitals yields reduced polar bonds of the An–Cl interaction giving similar values for both 1-Pu and 1-U, i.e. ~12% metal contribution (~88% polar) versus 6% (94% polar), respectively, Fig. 2. This agrees with the predicted V(r)/G(r) polarization values for these two bond types by QTAIM, ~81% and ~93%, for 1-U and 1-Pu, respectively, Table S3. We note that there is a very small amount of metal based \(\pi\)-contribution to the bonding as well, 2–5% depending on the symmetry and the identity of the ligand, Cl\(^-\) vs. OPcy$_3$, see Fig. S16. Interestingly, no semi-core 6p orbital involvement was found in the An–O$_2$ interactions, compared to previous results with mer-MBr$_3$(OPcy)$_3$ (M = Am, Nd, Ce).\(^{10}\) An overall agreement between localized orbitals and QTAIM is observed. However, the former fails to recover the increased orbital overlap in the An–O$_2$ bonds with respect to the An–Cl bonds, as predicted by QTAIM.

The takeaway message from the bonding analysis is that the coordination of Cl\(^-\) and OPcy$_3$ ligands to (UO$_2$)$_2$\(^+\), forming 1-U, affects the U=O$_2$ interaction more significantly than the (PuO$_2$)$_2$\(^+\)/1-Pu analogues. It is also observed that the OPcy$_3$ ligands have a stronger bonding interaction with the metal despite more covalent character of the U–Cl and Pu–Cl bonds, Table S3.

Turning to the solid-state electronic absorption spectroscopy of 1-Pu, the spectrum displays several weak excitations in the range of ~13,000–10,000 cm\(^{-1}\) (~760–1000 nm) and a broad charge transfer band >24,000 cm\(^{-1}\) (<400 nm). The characteristic excitation at ~12,050 cm\(^{-1}\) (831 nm) for (PuO$_2$)$_2$\(^+\) in 1M HClO$_4$ is not present in 1-Pu, Fig. 3.\(^{3}\) Attempts to record a solution phase spectrum showed evidence of reduction to Pu(IV), see Fig. S5. To help explain the electronic structure and spectroscopic properties of 1-Pu and 1-U, we employed spin-orbit (SO) CASSCF wavefunctions corrected by second order perturbation theory (PT2) compared with the gas-phase actinyl dication, (AnO$_2$)$_2$\(^+\). For the sake of clarity, the orbitals are described using their symmetry labels \(\sigma, \pi, \delta, \varphi\) for the \(\sigma\)–\(\delta\) configuration in (UO$_2$)$_2$\(^+\) offers an ideal starting point before moving to the \(\delta\)-\(\pi\) configuration in (PuO$_2$)$_2$\(^+\) and on to the 1-An metal complexes.

The SO-CASSPT2 calculations show that the equatorial coordination of ligands has a greater impact on 1-U than 1-Pu in terms of composition and assignment of their low-lying states with respect to the (AnO$_2$)$_2$\(^+\) models, see ES1 for more detailed information on the uranyl system.

Given the 5f$^2$ configuration of (PuO$_2$)$_2$\(^+\) and 1-Pu, the ground state term symbol of $^2H_{6\kappa}$ was confirmed to be correct due to the equal occupation the 5f$_5$ and 5f$_6$ orbitals. The position and assignment of the excited states were similar in both systems where triplet states predominate up to ~12,000 cm\(^{-1}\) (~830 nm). Excitations at higher energy which mainly correspond to singlet configurations appear at ~16,000 cm\(^{-1}\) (~625 nm), Fig. 3, Tables S1 & S2.

![Fig. 3. Solution phase UV-vis-NIR spectrum of (PuO$_2$)$_2$\(^+\) in 1M HClO$_4$ (calypso trace) and solid-state spectrum of 1-Pu (blue trace), at ambient temperature, with vertical bars corresponding to the SO-PT2 calculated states of the respective complexes.](image)
Although the ground state and excitations of (PuO$_2$)$_2$$_{2+}$ and 1-Pu seem similar, some striking differences are observed between the solution phase UV-vis-NIR spectrum of (PuO$_2$)$_2$$_{2+}$ and the solid-state spectrum of 1-Pu. The centrifugally forbidden excitation at ~12,039 cm$^{-1}$ (831 nm; $\lambda$ = 555 M$^{-1}$ cm$^{-1}$) predicted as 3$\Omega$ = 4g($^2$H$_4$) $\rightarrow$ 3$\Omega$ = 0$\gamma$ ($^3\Pi_a$) is attributed to a “one to one complex” $\Omega = 2, 3^\Pi$. Given that these electronic states have $\Delta I = 2$ ($J = 4$ and $J = 2$, respectively), this transition is considered to be hypersensitive in nature. Thus, the dramatic change observed in the peak at ~12,039 cm$^{-1}$ is explained by the presence of an inversion centre in 1-Pu, while a variety of non-centrosymmetric structures can be found in (PuO$_2$)$_2$$_{2+}$.

The non-centrosymmetric cis-PuO$_2$Cl$_2$(OPcy)$_2$ complex could exhibit the characteristic excitation at ~12,039 cm$^{-1}$, but a solution phase spectrum in CDCl$_3$ showed no such evidence, see Fig. 55. We note that the spectrum was recorded ~1 month after the synthesis was performed and showed evidence of some Pu(V), see ESI for details.

The OPcy$_3$ ligand offers a convenient handle in 31P NMR spectroscopy. Previous studies of uranyl-phosphine oxide complexes have observed cis/trans isomerization by 31P NMR spectroscopy. 11 Previously it was reported that PuO$_2$Cl$_2$(OPcy)$_3$, 1-Pu, resonated at 3$\delta$ $\sim$110.2 ppm, though some of the details are uncertain. 12 In our hands, 1-Pu displayed two paramagnetically shifted and broadened resonances at 3$\delta$ $\sim$5.6 and $\sim$111.0 ppm (CDCl$_3$) in an 1:3 ratio, respectively. It is expected that a cis or trans isomer would give different shifts as observed for the uranyl analogues, the paramagnetism of the (PuO$_2$)$_2$$_{2+}$ ion complicates a full interpretation, in addition to experimental limitations by radiological restrictions. Previous studies of trans-PuO$_2$Cl$_2$(OPPh$_3$)$_2$, 2-Pu, showed that only a single 31P resonance at room temperature was observed, ca. 3$\delta$ $\sim$144.5 ppm (CDCl$_3$), while two resonances attributed to the cis and trans isomers with little separation were observed at reduced temperature (ca. 3$\delta$ $\sim$185 and $\sim$187 ppm, respectively, 253 K). The reaction of [PuO$_2$Cl$_2$(THF)$_2$]+ with OPPh$_3$ showed a major resonance at 3$\delta$ $\sim$146 ppm (THF-d$_8$) which was attributed to a putative “PuO$_2$Cl$_2$(OPPh$_3$)$_2$” complex, while a second, smaller, resonance was observed at 3$\delta$ $\sim$16 ppm which was attributed to a “one to one complex” e.g. “[PuO$_2$Cl$_2$(OPPh$_3$)(THF)$_2$]$. When an excess of OPcy$_3$ in CDCl$_3$ was added to 1-Pu, not only were the two resonances still present at approximately the same shifts, but a third resonance at 3$\delta$ +55.4 ppm was observed, this value is near the value of free OPcy$_3$, 3$\delta$ +50.574 ppm (CDCl$_3$). 10

Conclusions

In summary the synthesis of trans-PuO$_2$Cl$_2$(OPcy)$_2$, 1-Pu, has been confirmed, crystallizing as a distorted octahedron with all homo ligands trans to one another, and offers a good structural comparison with its uranyl analogue, 1-U. Theoretical calculations show that the coordination of meridional ligands gives a larger effect on the axial An=O$_2$ interaction for 1-U than for 1-Pu. This claim of bond weakening is supported by both bonding and electronic structure analysis. Furthermore, QTAIM results showed that despite the prediction of higher covalency in the An–Cl bonds, the An–O$_2$ bonds are stronger based on the accumulation of electron density in the interatomic region. Due to the crystallographic inversion centre, the intense $^2\Delta g$ (J = 4) $\rightarrow$ 3$\Pi_a$ (J = 2) transition is defined as hypersensitive and the dramatic change observed in the peak at ~12,039 cm$^{-1}$ is explained by the presence of an inversion centre in 1-Pu, while a variety of non-centrosymmetric structures can be found in (PuO$_2$)$_2$$_{2+}$.


