



Plutonium nitrate chloro complexes: Ligand competition and computational metrics for assembly and bonding.

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Plutonium nitrate chloro complexes: Ligand competition and computational metrics for assembly and bonding.

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Four new [Pu(IV)(NO₃)_{6-n}Cl_n]²⁻ (n = 0, 2, 3) and [Pu(VI)O₂(NO₃)Cl₃]²⁻ containing materials were crystallized from acidic, aqueous media and structurally characterized. The anions are assembled via hydrogen and halogen bonding motifs, which are rationalized computationally. The Pu-NO₃ and -Cl bonds were probed using QTAIM and NLMO analyses and found to be polar and largely ionic.

Plutonium has remained central to the nuclear industry as historical production and separation efforts geared towards nuclear weapons production have transitioned into large-scale endeavours for the disposition of used nuclear fuels, decommissioned nuclear weapons, and for the remediation of contaminated legacy nuclear weapons testing and production sites.¹ Vital to the success of these efforts is a sound understanding of the fundamental chemistry of plutonium, particularly in aqueous media, and in the presence of anions relevant to separations and disposition (e.g. NO₃⁻ and Cl⁻).^{2, 3} Substantive challenges exist in this arena however, as complex redox (oxidation states from II to VII are known for Pu), hydrolysis and radiolysis behaviours give rise to unique coordination geometries.^{4, 5} As such, the synthesis and structural characterization of novel Pu compounds is a path forward not only for probing fundamental behaviour and properties, but also for informing predictive modelling efforts.

The ubiquity, utility, and importance of complexes of Pu with NO₃⁻ and Cl⁻ specifically has resulted in a well-developed understanding of Pu *solution* chemistry.⁶ However, the *solid state* chemistry remains under explored. In fact, there exists only a single reported example of a compound featuring both

Pu-NO₃ and -Cl bonds for which a crystal structure has been determined.⁷ This is somewhat surprising given that mixed chloride/nitrate compounds have been prepared and structurally characterized for U⁸⁻¹⁰ and Np.¹¹ For example, the [UO₂Cl₃(NO₃)]²⁻ anion can be prepared from uranyl nitrate in aqueous, acidic media (< 2M HCl) and assembled with 4-Xpyridinium (X = Cl, Br, I) cations.⁸ Moreover, efforts to explore the use of ionic liquids for advanced separations technologies has led to the formation of [UO₂Cl(NO₃)₂]⁻, [UO₂Cl₃(NO₃)]²⁻ and [UO₂Cl₄]²⁻ complexes, the presence of which can impact the extraction capability of the ionic liquid, yet may be controlled via the UO₂²⁺/NO₃⁻/Cl⁻ ratio.¹²

As part of our on-going efforts to expand the catalogue of structurally characterized Pu compounds produced from aqueous media, single crystals of **1**: (C₅H₅Ni)₂[Pu(NO₃)₆] · H₂O, **2**: (C₅H₆N)₂[Pu(NO₃)₃Cl₃], **3**: (C₅H₅Ni)₂[Pu(NO₃)₂Cl₄] and **4**: (C₅H₅NCl)₂[PuO₂(NO₃)Cl₃], were prepared by evaporation from acidic solutions and are assembled via hydrogen and halogen bonds donated by 4-Xpyridinium cations (4XPyH⁺). These materials were synthesized from a Pu IV or VI chloride stock solution (in 6M HCl) that was prepared from a Pu nitrate precursor. In short, PuO_{2(s)} was dissolved in concentrated HNO_{3(aq)} and the resulting solution was reduced to near dryness. Concentrated HCl_(aq) was added (while hot and at three separate intervals) to destroy the NO₃⁻ and any NO₂⁻ species. This process is a standard protocol in our laboratory (and others¹³) and it is therefore surprising that any nitrate (presumably at very low concentration) would remain and be capable of outcompeting the Cl⁻ anions for coordination. The coordination affinity of Pu⁴⁺ for nitrate is of course higher than that of chloride (whereas the opposite is true for Pu⁶⁺),^{14, 15} yet the differences in relative concentrations are large and thus, competitive binding was unexpected. The high ionic strength of the media (and therefore non-ideal speciation behaviour) is likely responsible the formation of **1-4**. While somewhat speculative at present, these sentiments are at the core of our efforts to probe Pu speciation and crystallization from aqueous Cl⁻/NO₃⁻ media.

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The remainder of this Communication has a structural focus as the unexpected formation of novel coordination geometries provides an opportunity to describe assembly motifs and Pu-ligand bonding characteristics, both of which may be realized computationally using electrostatic potential (ESP) maps and the Quantum Theory of Atoms in Molecules (QTAIM) approach, respectively, based on density functional theory (DFT) calculations.

Compound **1** contains $[\text{Pu}(\text{NO}_3)_6]^{2-}$ anions that form chains along [100] *via* intermolecular $\text{N}-\text{O}\cdots\text{O}_{(\text{nitrate})}$ contacts between the coordinated nitrate anions (Figure S6). Each chain is in turn linked by a hydrogen bonding network (via lattice water molecules and 4IPyH^+ cations) to form a 3D supramolecular structure that contains pseudo channels (Figures S5 and S7). The 4IPyH^+ cations occupy the channels and further stabilize the arrangement of the anions *via* $\text{C}-\text{I}\cdots\text{O}_{(\text{nitrate})}$ halogen bonds. The distribution of the ESP on the $[\text{Pu}(\text{NO}_3)_6]^{2-}$ anion is symmetric, and displays regular, well-defined non-covalent interaction (NCI) acceptor sites (the O atoms, at -624 kJ mol^{-1}) on the 0.001 au isodensity surface. The combined effects of the anion symmetry and dual donating ability of the 4IPyH^+ cations likely promotes the 3D connectivity.

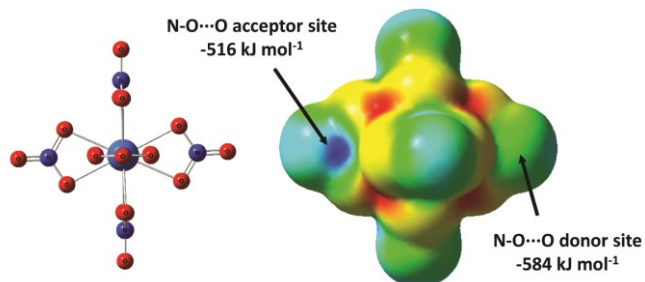


Figure 1. The electrostatic potential of the $[\text{Pu}(\text{NO}_3)_6]^{2-}$ anion in **1** mapped on an 0.001 au isodensity surface. The color scale represents a gradient from -667 kJ mol^{-1} (red) to -509 kJ mol^{-1} (blue).

The $[\text{Pu}(\text{NO}_3)_3\text{Cl}_3]^{2-}$ anions in **2** are charge balanced by HPyH^+ cations to form a molecular structure without any substantive supramolecular connectivity (Figure S8). The chloro ligands have a larger (more negative) ESP relative to the NO_3^- ligands and accordingly, are the best acceptor sites for the $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds that are donated by the HPyH^+ cations (Figure 2 and S9). Interestingly, the structure of **2** is of lower supramolecular connectivity than **1** despite the Cl^- ligands in **2** being a stronger NCI acceptor site (via comparison of the ESPs) than the NO_3^- ligands in **1**. The cause of this is in part due to the HPyH^+ cations being capable of donating only a single hydrogen bond, yet perhaps more relevant, is the asymmetry of the $[\text{Pu}(\text{NO}_3)_3\text{Cl}_3]^{2-}$ anion.

The $[\text{Pu}(\text{NO}_3)_2\text{Cl}_4]^{2-}$ anions in **3** feature a fourth Cl^- ligand (Figure 3) and are assembled by 4IPyH^+ cations. The sides of the chloro ligands are better NCI acceptors (-657 kJ mol^{-1} , Table S6) relative to the regions coaxial (-605 kJ mol^{-1}) and as such, form bifurcated $\text{N}-\text{H}\cdots\text{Cl}/\text{Cl}$ hydrogen bonds with the 4IPyH^+ cations (Figure S11). The 4IPyH^+ cations go on to form $\text{C}-\text{I}\cdots\text{O}$ halogen bonds with the nitrate ligands on neighbouring anions to give rise to infinite chains. Here, we note that the NCI acceptor sites

are more polarized relative to those in **2** (Figures 2 and 3). The distribution (and larger magnitude) of ESP in this region is likely due to the symmetry of the $[\text{Pu}(\text{NO}_3)_2\text{Cl}_4]^{2-}$ anion as the NO_3^- ligands in **2** are *trans* to the Cl^- ligands and likely effect the degree of polarization.

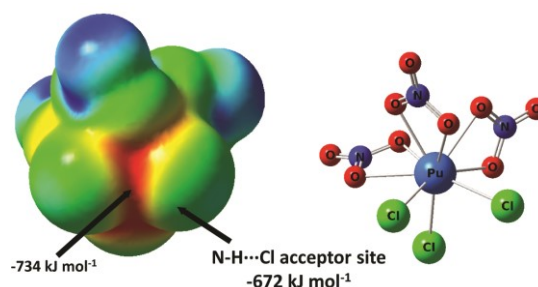


Figure 2. The electrostatic potential of the $[\text{Pu}(\text{NO}_3)_3\text{Cl}_3]^{2-}$ anion in **2** mapped on an 0.001 au isodensity surface. The color scale represents a gradient from -740 kJ mol^{-1} (red) to -522 kJ mol^{-1} (blue).

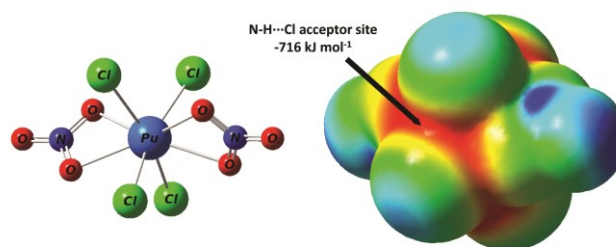


Figure 3. The electrostatic potential of the $[\text{Pu}(\text{NO}_3)_2\text{Cl}_4]^{2-}$ anion in **3** mapped on an 0.001 au isodensity surface. The color scale represents a gradient from -722 kJ mol^{-1} (red) to -570 kJ mol^{-1} (blue).

Compound **4** is the lone example in this series that features the $[\text{Pu}(\text{VI})\text{O}_2]^{2+}$ cation and we note that $\text{Pu}(\text{VI})$ was intentionally targeted as $\text{KBrO}_3(s)$ was used to oxidize the Pu to $6+$. The $[\text{PuO}_2(\text{NO}_3)_2\text{Cl}_3]^{2-}$ anions in **4** are flanked by 4ClIPyH^+ cations, which donate bifurcated $\text{N}-\text{H}\cdots\text{Cl}/\text{Cl}$ and $\text{N}-\text{H}\cdots\text{Cl}/\text{O}_{(\text{nitrate})}$ hydrogen bonds. Subsequently, a $\text{C}-\text{Cl}\cdots\text{Cl}$ halogen bonding network forms between the 4ClIPyH^+ cations to give rise to a finite chain motif (Figure S12), which is isomorphous with the corresponding uranyl analogue.⁸ The magnitude of the ESP on the $[\text{PuO}_2(\text{NO}_3)_2\text{Cl}_3]^{2-}$ anion is larger than each of the $\text{Pu}(\text{IV})$ anions, and is likely due to the combined contribution of the 3:1 $\text{Cl}^-/\text{NO}_3^-$ ratio and the presence of the electron donating axial oxo ligands. We note similarities between the magnitude and distribution of the ESP on the $[\text{PuO}_2(\text{NO}_3)_2\text{Cl}_3]^{2-}$ and the related $[\text{UO}_2(\text{NO}_3)_2\text{Cl}_3]^{2-}$ (Figure S21) and $[\text{PuO}_2\text{Cl}_4]^{2-}$ anions.¹⁶

Overall, the ESP magnitude on the Pu^{4+} anions increases with the replacement of the NO_3^- ligands for Cl^- ligands. The latter are better NCI acceptors due to their more negative and anisotropic distribution of ESP, which results in the formation of distinct and 'directional' acceptor sites. Whereas the identity of the ligand affects the physical distribution of the ESP, the symmetry of the local coordination environment also plays an important role. For example, the degree of polarization about

the chloro ligands in **2** is less than that in **3** as the *trans* NO₃⁻ in the former offsets the polarization of the Cl⁻. The symmetry of the Pu anion and its ESP clearly influences the resulting supramolecular connectivity, yet the extent to which these characteristics may be exploited to promote a targeted structure type is unclear and is an area of active pursuit within our group.

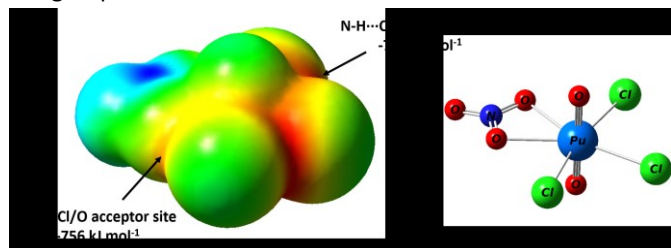


Figure 4. The electrostatic potential of the [PuO₂(NO₃)Cl₃]²⁻ anion in **4** mapped on an 0.001au isodensity surface. The color scale represents a gradient from -793 kJ mol⁻¹ (red) to -551 kJ mol⁻¹ (blue).

The structures described herein contribute to broader efforts to delineate structural and electronic trends across the 5f block. The approach of restricting speciation to a limited suite of anions, e.g. [AnO₂Cl₄]²⁻ (An = U, Np, Pu), that are appropriate for assembly with any number of judiciously selected pyridinium cations provides a means to systematically promote desired structure types for targeted analyses. For instance, our previous efforts reported twelve (eight novel) actinyl tetrachloride containing materials that served as a platform for evaluating supramolecular assembly, i.e. rationalizing acceptor-donor pairings, structural disposition and quantifying strengths of NCl_s.¹⁶

Whereas the crystallization of **1-4** was admittedly unexpected (which seemingly contradicts the theme of systematic assembly within the previous paragraph!), the coordination of NO₃⁻ and Cl⁻ ligands by Pu, as well as the rather straightforward structure types that resulted, provide an opportunity to probe the extent of the covalency of the Pu-ligand bonds as this topic is of practical¹⁷⁻¹⁹ and fundamental interest.²⁰⁻²⁵ Here, we have utilized QTAIM and Natural Localized Molecular Orbital (NLMO) analyses to highlight the nature of the Pu-NO₃, Pu-Cl and Pu=O_{yl} bonds and we offer a description of the hybrid atomic orbitals (HAO) that comprise each bonding interaction thereof.

The QTAIM analysis revealed that the Pu-Cl and Pu-NO₃ bonds are polar and primarily ionic (**Table 1**). The electron density (ρ) parameter and the Laplacian ($\nabla^2\rho$) that describe the former are both positive, which is typical of an ionic bond,²⁶ and decrease from **2**: [Pu(NO₃)₃Cl₃]²⁻ < **3**: [Pu(NO₃)₂Cl₄]²⁻ < **4**: [PuO₂(NO₃)Cl₃]²⁻. The electronic energy density (H) value is negative and on the order of 10⁻², which also indicates the Pu-Cl bond is primarily ionic, but may have (due to the negative sign) a minor covalent contribution. Moreover, the average ratio of the kinetic (G) and potential (V) energy densities are 1.28, which also suggests an ionic bond with some covalent character.²⁶ Finally, the delocalization index (δ) – a measure of bond order^{27, 28} – increases from **4** < **2** < **3**, which suggests the

Pu-Cl bonds in **3** are the most covalent. This is consistent with the ESP about the Cl ligands in **2** and **3** and highlights the effect of the *trans* NO₃⁻ in **2**. For the Pu-NO₃ bonds we note opposite trends in ρ , $\nabla^2\rho$, and H as the bonding interactions (Cl⁻ vs NO₃⁻) work in opposition. There is no covalent contribution to the bonding as H is on the order of 10⁻³ (essentially zero) and the average ratio of the kinetic and potential energy densities is 1.09, which are both consistent with ionic bonds. We note here the topological parameters of **4** do not trend with those of **1-3**, which speaks to the influence of the coordination geometry as the strong, covalently bound 'yl' oxo ligands impart an influence in the equatorial plane that is not (for obvious reasons) observed in the Pu⁴⁺ systems.

Table 1. Averaged QTAIM parameters for the Pu-Cl and Pu-NO₃ bonds in **1-4**.

Pu-Cl	ρ	$\nabla^2\rho$	H_{BCP}	$\delta(A, B)$	$\frac{ V_{BCP} }{G_{BCP}}$
2	0.0673	0.1535	-0.0152	0.5683	1.283
3	0.0670	0.1478	-0.0149	0.5959	1.287
4	0.0564	0.1360	-0.0098	0.4948	1.223
Pu-NO ₃					
1	0.0508	0.1857	-0.0047	0.2531	1.092
2	0.0533	0.1971	-0.0054	0.2657	1.098
3	0.0565	0.2070	-0.0067	0.2642	1.113
4	0.0459	0.1778	-0.0029	0.2242	1.059
Pu=O _{yl}					
4	0.3232	0.3557	-0.2897	1.97	1.765

The NLMOs representing the bonds are strongly polarized toward the ligands, with an average of 86% / 92% of the orbital density on Cl / nitrate, and therefore consistent with a predominantly ionic Pu-Cl and Pu-NO₃ bond picture (**Tables S9** and **S10**). The Cl HAOs are the primary constituents of the Pu-Cl bonds in **2-4** (at an avg. of 86%) and are composed of both s (~33%) and p (~67%) character. On the Pu side the HAOs participating in Pu-Cl bonding have mixed s (~17%), d (~50%) and f (~34%) character. The Pu HAOs participating in Pu-nitrate bonding have mixed s (~13%), d (~47%) and f (~39%) character. We note that one of the Cl ligands (Cl14 in **Figure S13**) in **2** features two bonding interactions, which is suggestive of back bonding. In contrast, each Pu-O_{yl} bond in **4** is comprised of three bonding NLMOs (consistent with a triple bond) that feature more evenly shared contributions from O and Pu at ~65% and ~35%, respectively. These results when taken in context with the QTAIM analysis highlight the known covalent nature of the Pu-O_{yl} bond.²⁹ Further, the [UO₂(NO₃)Cl₃]²⁻ anion was also subjected to QTAIM and NLMO analyses (see Supporting Information) and demonstrates a covalent (axial) and ionic (equatorial) bonding picture similar to that of the [PuO₂(NO₃)Cl₃]²⁻ anion.

In total, four novel materials containing [Pu(IV)(NO₃)_{6-n}Cl_n]²⁻ (n = 0, 2, 3) and [Pu(VI)O₂(NO₃)Cl₃]²⁻ anions were prepared and are the first structurally characterized examples where Pu is solely coordinated by both NO₃⁻ and Cl⁻ ligands. The synthesis of these materials (being from a Pu chloride stock) is of note as

competition for Pu coordination by NO_3^- and Cl^- is observed, which not only speaks to the complexity of Pu speciation in high ionic strength media, but may also suggest the second sphere NCl's play a role in stabilizing these unique coordination environments. The supramolecular nature of these assemblies were therefore rationalized electrostatically and the resulting dimensionality was found to be an interplay between the magnitude of the ESP and symmetry of the anion and the identity of the pyridinium cation. Beyond these structural implications, this system proved a fertile forum for probing the nature of the Pu- NO_3 , Pu-Cl and Pu = O_{yl} bonds. The QTAIM and NLMO analyses revealed the former bonds to be polar and dominated by ionic contributions whereas the Pu= O_{yl} bond is strong and covalent. Looking ahead, this synthetic strategy and supramolecular approach will be exploited as a means to systematically explore Pu (and actinide) bonding.

Conflicts of interest

There are no conflicts to declare.

Notes and references

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