SUPPORTING INFORMATION

Plutonium chlorido nitrato complexes: Ligand competition and computational metrics for assembly and bonding.

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1. Synthesis

Caution! ^{239}Pu ($t_{1/2}$ = 2.4 x 10^4 y) is an α and γ emitting radionuclide, is hazardous and poses a health risk. All experiments and manipulations were performed in a facility designed and designated for handling radionuclides. Dispersible solids were handled and manipulated in a negative-pressure radiological glovebox, whereas single-crystals were handled in radiological fume hoods after being coated with Krytox grease or Paratone-N oil.

The reagents used in this study were purchased and used without further purification: pyridine (Sigma-Aldrich, 99%), 4-chloropyridine · HCl (Sigma-Aldrich, 99%) and 4-Iodopyridine (Sigma-Aldrich, 96%).

Pu(IV) Stock Solution

$^{239}PuO_{2(s)}$ was boiled in concentrated $HNO_{3(aq)}$ and a minimal volume of $HF_{(aq)}$ until dissolved. The volume of this emerald green solution was reduced to near dryness and concentrated $HCl_{(aq)}$ was added to the hot moist solid. A reddish-orange solution resulted and was boiled to near dryness. $HCl_{(aq)}$ was again added and this process was repeated three times. The solution was cooled to room temperature and hydrogen peroxide (30%) was added to drive the oxidation state of the Pu to +3. The midnight blue solution was left open to the air to oxidize such that a crimson red solution remained. The oxidation state of the Pu was verified to be +4 by UV-Vis absorbance spectroscopy and the concentration was determined to be 35 mg Pu/mL by high resolution γ-spectroscopy. The total volume of the stock solution was 2.0mL. We note that this solution must have contained trace levels of nitrate anions per the synthetic results (below), which means the additions of $HCl_{(aq)}$ were insufficient to destroy all of the nitrate species.

Synthesis of 1 - 3

1: A 250 μL aliquot of the $^{239}Pu(IV)$ stock solution was added into a vial containing 500μL of 6M HCl and 8 molar equivalents (based on Pu) of 4-iodopyridine.

2: A 350 μL aliquot of the $^{239}Pu(IV)$ stock solution was added into a vial containing 200μL of 6M HCl and 8 molar equivalents (based on Pu) of pyridine.

3: A 250 μL aliquot of the $^{239}Pu(IV)$ stock solution was added into a vial containing 440μL of 6M HCl and 8 molar equivalents (based on Pu) of 4-chloropyridine · HCl.

Crystals of **1**-**3** that were suitable for crystallographic analysis formed over the course of several weeks and were harvested.

Pu(VI) Stock Solution

The same process used to prepare the Pu(IV) stock solution was utilized here, yet after the third addition of $HCl_{(aq)}$, the solution was taken to near dryness and 5mL of H_2O were added. The solution was heated, stirred and an excess of $KBrO_{3(s)}$ was added. The oxidation of Pu(IV) → Pu(VI) occurred over a period of 5 minutes and upon completion, the volume of the solution was reduced to near dryness. The moist solids were dissolved in 2 mL of concentrated $HCl_{(aq)}$. The oxidation state of the Pu was verified to be +6 by UV-Vis absorbance spectroscopy and the concentration was determined to be 219 mg Pu/mL by high resolution γ-spectroscopy.

Synthesis of 4

A 80μL aliquot of the ^{239}Pu(VI) stock solution was added to a two dram vial that contained two molar equivalents (based on Pu) of crystalline 4-chloropyridine · HCl. Crystals suitable for crystallographic analysis formed over the course of several weeks and were harvested. Reaction yields were not obtained.

2. X-ray Crystallography

Sample Preparation

All manipulations were performed in a radiological fume hood designated for handling transuranic radioisotopes. Single crystals of **1** – **4** were coated in Paratone-N oil and cut to an appropriate size for the diffraction experiment. The crystals were in turn mounted onto the MiTeGen MicroMount™ and coated in Krazy™ glue. In the case of **3** and **4**, a clear heat sealable tube (manufactured by Vention® Medical) made of polyphenylene ether was placed over the MicroMount™ and copper post and affixed with epoxy.

Experiment Details

Reflection data of **1** and **2** were collected using 0.5°ω scans at 110(2)K on a Bruker Quazar diffractometer equipped with an APEX II CCD detector with a Mo Kα IμS source whereas data of **3** and **4** were collected using 0.5°ω and φ scans at 296(2)K on a Bruker D8 Venture diffractometer equipped with a Photon 100 CMOS detector with a Mo Kα source equipped with a triumph monochromator and Ag IμS source (**Table S1**). All data were reduced and corrected for absorption (SADABS[1] or TWINABS) using the APEX III software suite.[2] The data were solved using direct methods via SHELXS[3] and refined using SHELXL-14[4] within the WINGX software suite.[5] Publication materials were prepared using EnCifer V.1.6.1[6] and figures of title compounds were made using CrystalMaker V.10.2.1.[7]

All of the non-hydrogen atoms in **1** – **4** were located using difference Fourier maps and refined anisotropically. The H atoms associated with the carbon and nitrogen atoms of the 4-X-pyridinium (X = H, Cl, I) cations were located in difference Fourier maps, but were placed in calculated positions and allowed to ride on their parent atoms. We note that the H atoms associated with the nitrogen atoms in **1-4** were modeled, distance restrained (DFIX) and refined isotropically. The H atom on N2 in **4** was placed in a calculated position and allowed to ride on its parent atom. The pyridinium ring in **2** was disordered over two positons and was therefore modeled using a Part command. Subsequently, the N atoms were treated with ISOR restraints to account for high Ueq values.

We are thankful to Dr. Ginger Sigmon of the Department of Civil and Environmental Engineering and Earth Sciences at the University of Notre Dame for the data collections of **1** and **2**.

Table S1. Selected crystallographic data from compounds **1-4**.

	Compound 1	**Compound 2**	**Compound 3**	**Compound 4**
Formula	$C_{10}H_{10}I_2N_8O_{20}Pu$	$C_{10}H_{12}Cl_3N_5O_9Pu$	$C_{10}H_8Cl_4I_2N_4O_6Pu$	$C_{10}H_{10}Cl_5N_3O_5Pu$
Formula mass	1058.06	694.60	917.80	671.46
λ	0.71073 Å	0.71073 Å	0.71073 Å	0.56086 Å
Temperature of Data Collection	110(2)K	110(2)K	298(2)K	298(2)K
Crystal Color and Habit	Dark Green Prismatic	Orange Blade	Dark Red Blade	Yellow Blade
Size	0.100 x 0.075 x 0.050	0.100 x 0.075 x 0.050	0.100 x 0.075 x 0.050	0.100 x 0.075 x 0.050
Space Group	*P2₁/n*	*P2₁/c*	*P-1*	*P-1*
a (Å)	8.7845(7)	17.2683(14)	9.8096(8)	6.7493(5)
b (Å)	12.3118(10)	7.7622(6)	10.1402(8)	10.8107(9)
c (Å)	12.6497(11)	15.1117(11)	11.5033(9)	14.1715(11)
α (°)	90.00	90.00	73.4160(10)	73.657(2)
β (°)	96.4470(10)	97.598(2)	82.3640(10)	81.412(2)
γ (°)	90.00	90.00	87.1000(10)	75.206(2)
Volume (Å^3)	1359.45(19)	2007.8(3)	1086.83(15)	956.00(13)
D_{calc} (Mg m^{-3})	2.585	2.298	2.805	2.333
Z	2	4	2	2
μ (mm^{-1})	4.794	3.735	6.398	5.149
No. of reflections measured	16668	9538	12875	18087
No. of independent reflections	3374	4469	4809	4740
R_{int}	0.0598	0.0326	0.0301	0.0382
Final R_1 values ($I > 2\sigma(I)$)	0.0338	0.0209	0.0361	0.0646
Final wR_2 (F^2) values ($I > 2\sigma(I)$)	0.0732	0.0508	0.0881	0.1118
Goodness of fit on F^2	1.005	1.236	1.045	1.333
CCDC number	1852697	1852698	1852699	1852700

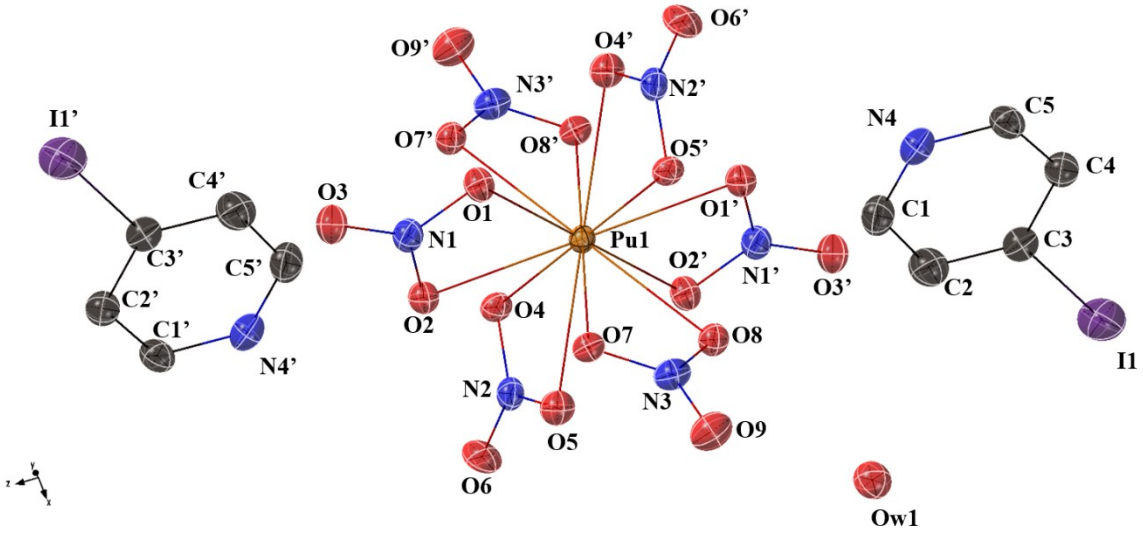

Figure S1. The structure of **1** with the thermal ellipsoids drawn at the 50% probably level.

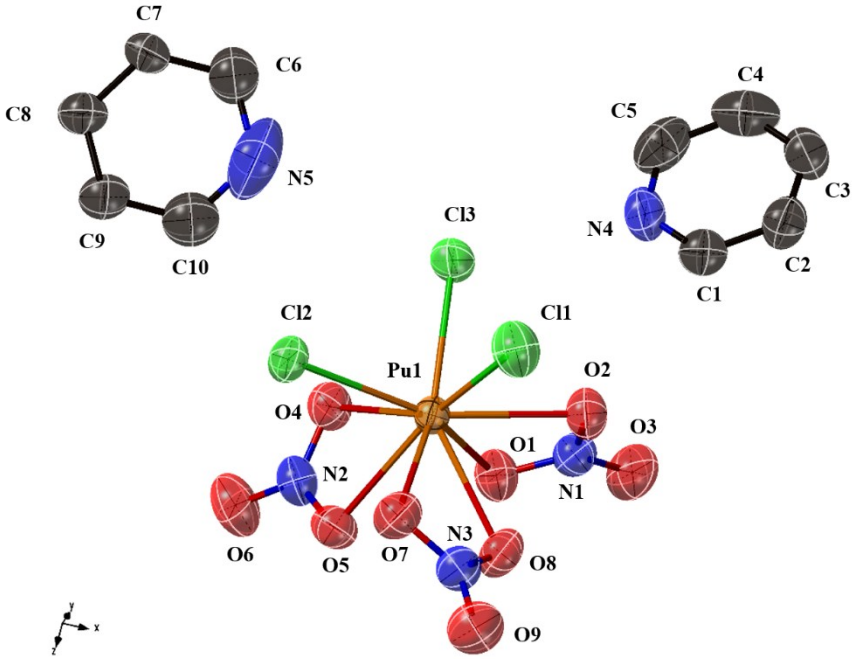

Figure S2. The structure of **2** with the thermal ellipsoids drawn at the 50% probably level.

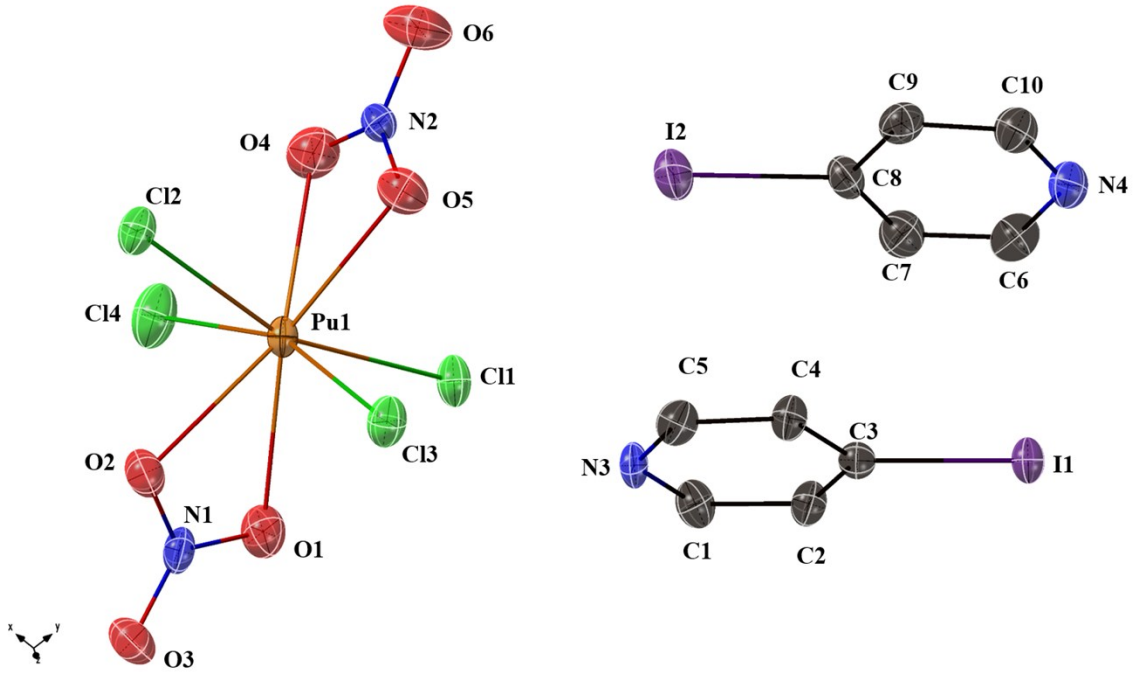

Figure S3. The structure of **3** with the thermal ellipsoids drawn at the 50% probably level.

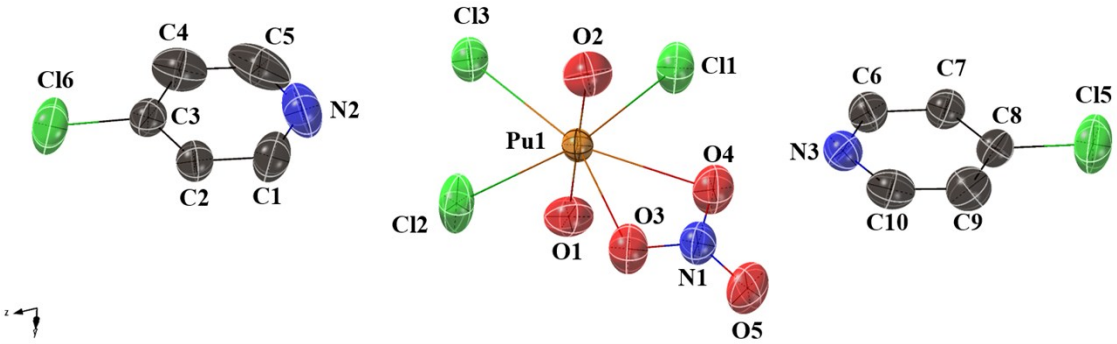

Figure S4. The structure of **4** with the thermal ellipsoids drawn at the 50% probably level.

3. Bond Lengths and Interaction Parameters

Table S2. Selected bond lengths and angles that describe the local coordination geometry about each Pu anion in **1**-**4**.

Anion	Bond	Length (Å)	Angle	Degree (°)
1: $[Pu(NO_3)_6]^{2-}$	O(1)-Pu(1)	2.500(4)	O(2)-Pu(1)-O(1)	51.23(12)
	O(2)-Pu(1)	2.473(4)	O(4)-Pu(1)-O(5)	51.27(11)
	O(4)-Pu(1)	2.470(4)	O(8)-Pu(1)-O(7)	51.35(12)
	O(5)-Pu(1)	2.498(4)		
	O(7)-Pu(1)	2.503(4)		
	O(8)-Pu(1)	2.480(3)		
2: $[PuCl_3(NO_3)_3]^{2-}$	O(1)-Pu(1)	2.446(3)	O(1)-Pu(1)-O(2)	51.7(1)
	O(2)-Pu(1)	2.497(3)	O(4)-Pu(1)-O(5)	51.49(9)
	O(4)-Pu(1)	2.468(3)	O(8)-Pu(1)-O(7)	51.17(9)
	O(5)-Pu(1)	2.450(3)	Cl(1)-Pu(1)-Cl(2)	88.75(4)
	O(7)-Pu(1)	2.475(3)	Cl(1)-Pu(1)-Cl(3)	83.79(4)
	O(8)-Pu(1)	2.448(3)	Cl(2)-Pu(1)-Cl(3)	88.03(3)
	Cl(1)-Pu(1)	2.5996(10)	O(8)-Pu(1)-O(7)	51.49(9)
	Cl(2)-Pu(1)	2.6143(9)	O(1)-Pu(1)-O(2)	51.17(9)
	Cl(3)-Pu(1)	2.6263(10)	Cl(1)-Pu(1)-Cl(2)	88.75(4)
3: $[PuCl_4(NO_3)_2]^{2-}$	O(1)-Pu(1)	2.430(5)	O(1)-Pu(1)-O(2)	51.95(18)
	O(2)-Pu(1)	2.441(5)	O(4)-Pu(1)-O(5)	51.84(16)
	O(4)-Pu(1)	2.451(5)	Cl(3)-Pu(1)-Cl(4)	162.09(6)
	O(5)-Pu(1)	2.467(5)	Cl(3)-Pu(1)-Cl(2)	89.10(5)
	Pu(1)-Cl(3)	2.5995(15)	Cl(4)-Pu(1)-Cl(2)	95.07(5)
	Pu(1)-Cl(4)	2.6011(15)	Cl(3)-Pu(1)-Cl(1)	92.08(6)
	Pu(1)-Cl(2)	2.6133(16)	Cl(4)-Pu(1)-Cl(1)	89.34(6)
	Pu(1)-Cl(1)	2.6142(18)	Cl(2)-Pu(1)-Cl(1)	161.88(7)
4: $[PuO_2Cl_3(NO_3)]^{2-}$	O(1)-Pu(1)	1.732(8)	O(1)-Pu(1)-O(2)	179.2(4)
	O(2)-Pu(1)	1.744(8)	O(3)-Pu(1)-O(4)	50.0(2)
	O(3)-Pu(1)	2.502(8)	Cl(2)-Pu(1)-Cl(3)	84.40(8)
	O(4)-Pu(1)	2.549(7)	Cl(1)-Pu(1)-Cl(3)	82.97(8)
	Cl(1)-Pu(1)	2.680(3)	Cl(2)-Pu(1)-Cl(3)	84.40(8)
	Cl(2)-Pu(1)	2.669(3)		
	Cl(6)-Pu(1)	2.708(3)		

Table S3. Selected non-covalent interaction parameters from **1**-**4**.

	Interaction	**Distance (Å)**	**Angle (°)**
1	N3-O9 ··· O9’	2.932(5)	90.2(3)
	C3-I1 ··· O2	3.274(4)	164.91(16)
	C3-I1 ··· O7	3.360(4)	144.22(16)
	N4-H4a ··· Ow1	2.762(6)	159
	N2-O6 ··· Ow1	2.762(6)	118.9(3)
2	C3-I1 ··· O5	3.072(5)	170.1(2)
	C8-I2 ··· O2	3.582(5)	154.6(2)
	N3-Hn1 ··· Cl2	3.286(6)	140(5)
	N3-Hn1 ··· Cl3	3.298(6)	130(5)
	N3-Hn1 ··· O6	3.036(8)	109
	N4-Hn2 ··· Cl1	3.334(7)	116(6)
	N4-Hn2 ··· Cl4	3.268(6)	146(6)
3	N5-H8a ··· Cl3	3.487(6)	163
	N4-H4 ··· Cl3	3.228(4)	154
	N4-H4 ··· Cl1	3.536(5)	126
4	C8-Cl4 ··· Cl4	3.237(5)	138.1(4)
	N3-H3 ··· O3	2.877(13)	141
	N3-H3 ··· Cl1	3.367(11)	138
	N2-H2a ··· Cl3	3.174(12)	154
	N2-H2a ··· Cl2	3.53(1)	122

4. Figures of Compounds 1 – 4

Compound 1: $(C_5H_5NI)_2[Pu(NO_3)_6] \cdot 2H_2O$

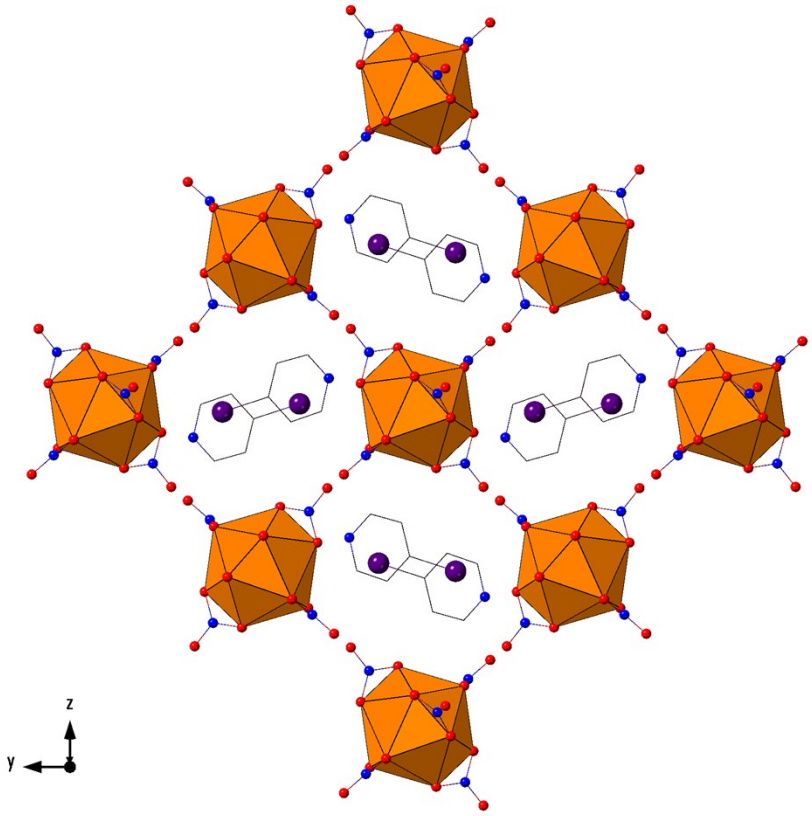

Figure S5. The structure of **1** as shown down the [100] direction. The water molecules have been omitted for clarity.

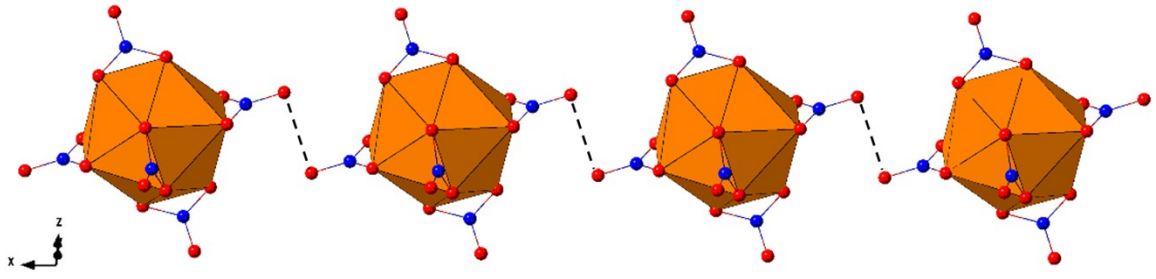

Figure S6. The $[Pu(NO_3)_6]^{2-}$ anions in **1** form chains along [100] via N-O···$O_{(nitrate)}$ intermolecular contacts.

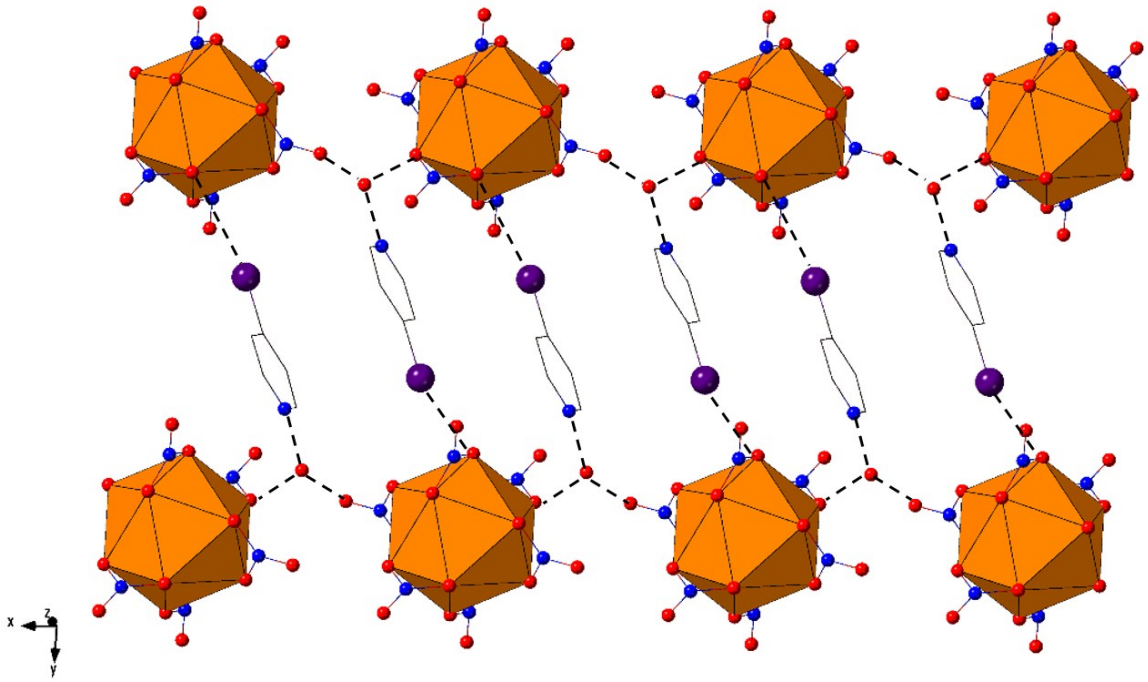

Figure S7. Hydrogen and halogen bonds in **1** link parallel chains of $[Pu(NO_3)_6]^{2-}$ anions.

Compound 2: $(C_5H_6N)_2[PuCl_3(NO_3)_3]$

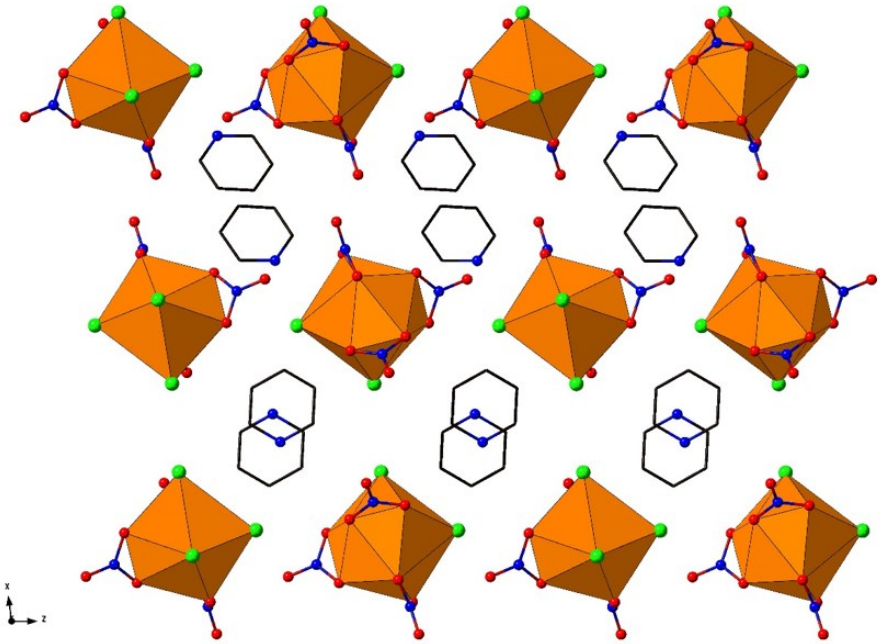

Figure S8. A view down the [010] direction of the $HPyH^+$ cations and $[PuCl_3(NO_3)_3]^{2-}$ anions in **2**.

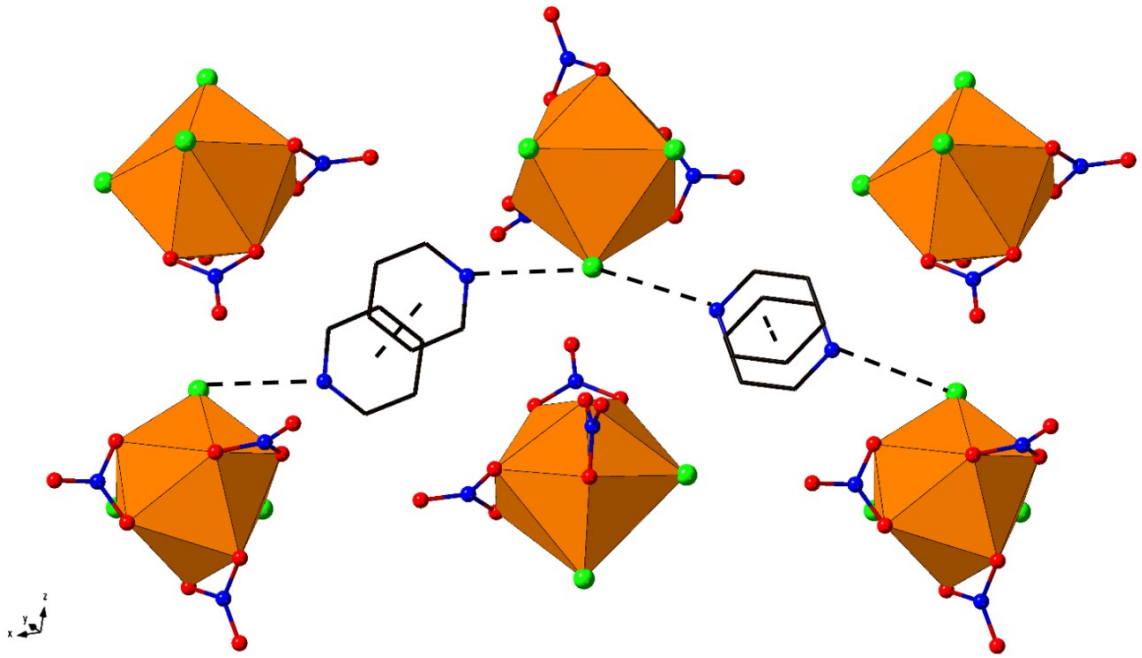

Figure S9. Hydrogen bonds and offset-π interactions in **2** stem from the $HPyH^+$ cations and link the $[PuCl_3(NO_3)_3]^{2-}$ anions.

Compound 3: $(C_5H_5NI)_2[PuCl_4(NO_3)_2]$

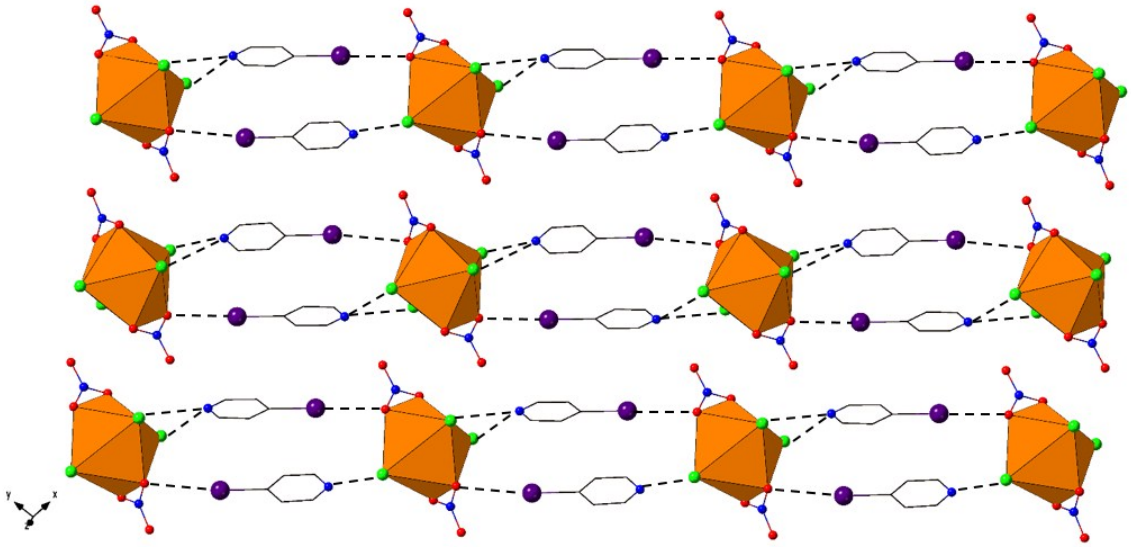

Figure S11. Hydrogen and halogen bonds in **3** stem from the $4IPyH^+$ cations and link the $[PuCl_4(NO_3)_2]^{2-}$ anions into parallel and planar chains to form a pseudo sheet.

Compound 4: $(C_5H_5NCl)_2[PuO_2Cl_3(NO_3)]$

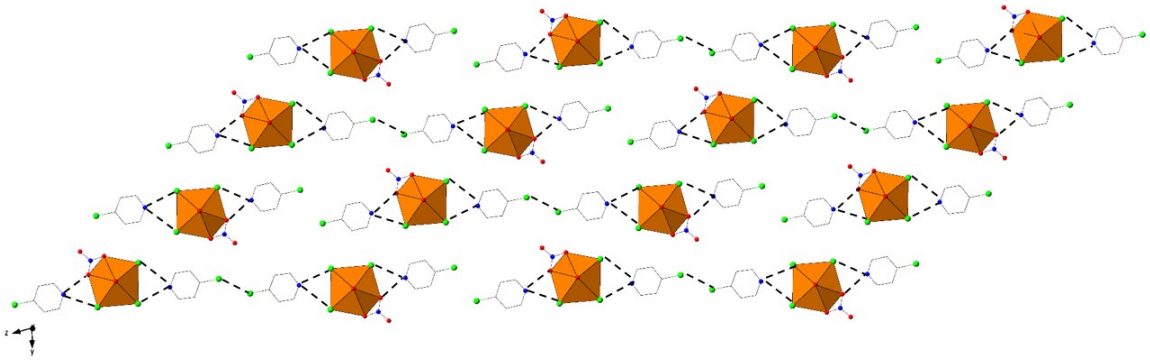

Figure S12. The $4ClPyH^+$ cations in **4** form hydrogen bonds with the $[PuO_2Cl_3(NO_3)]^{2-}$ anions. The chloro substituents go on to form C-Cl···Cl halogen bonds (dashed lines) to form finite chains.

5. Computational Details and Results

The M06-2X level of theory[8] and the following basis sets: Pu - 60MWB-SEG + ECP-60MWB;[9-11] I - def2-TZVP + ECP; Cl, C, N, O, H - def2-TZVP[12] were used in the electrostatic potential (ESP), Quantum Theory of Atoms in Molecules (QTAIM) and Natural localized molecular orbital (NLMO) calculations. Atomic coordinates were taken directly from the crystallographic data and the structures were not optimized. All calculations were performed using Gaussian 09 (rev. D.01)[13] (with the Gaussview V5.01 interface[14]) save for the QTAIM analysis, which was performed using AIMALL.[15]

The electrostatic potential of the $[Pu(NO_3)_6]^{2-}$, $[PuCl_3(NO_3)_3]^{2-}$, $[PuCl_4(NO_3)_2]^{2-}$, $[PuO_2Cl_3(NO_3)]^{2-}$ anions from **1** – **4** were calculated and mapped on a 0.001 au isodensity surface so that the crystallographically observed structural motifs could be rationalized and the non-covalent interaction (NCI) acceptor-donor properties characterized. The NCIs were also treated with a QTAIM analysis so that the nature of each interaction could be assessed in a manner that is somewhat independent of the Coulombic contribution. The plutonium/ligand bonding interactions were also investigated computationally using QTAIM and NLMO analyses to probe the covalent character of each bond and to elucidate the atomic orbital contributions that comprise each bonding interaction.

Electrostatic Potential

Table S4. Electrostatic potential values at various regions on the $[Pu(NO_3)_6]^{2-}$ anions. The atom labels correspond to those depicted in Figure S12.

Coaxial to the bond axis	**Potential in kJ mol-1**
O6	-544
O9	-544
O12	-551
O19	-544
O22	-544
O25	-551
Perpendicular to the bond axis (top of O atom – blue region)	
O6	-516
O19	-517
Perpendicular to the bond axis (bottom of O atom)	
O6	-586
O19	-582
Regions between the NO_3^- ligands	
	-667
	-668
	-664
	-667
NCI Acceptor Regions	
O4 (accepts C3-I1 ··· O7)	-625
O7 (accepts C3-I1 ··· O2)	-622

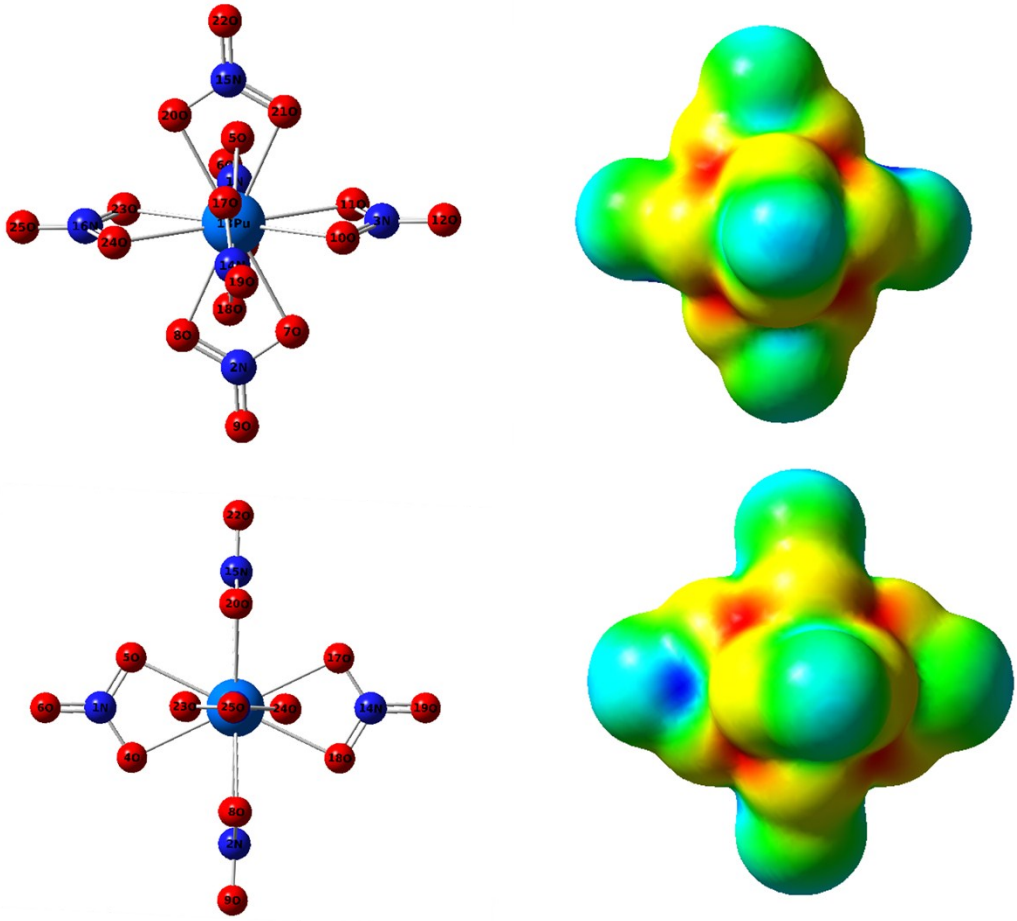

Figure S12. The electrostatic potential of the $[Pu(NO_3)_6]^{2-}$ anion from **1** is mapped on an 0.001au isodensity surface. The color scale represents a gradient from high potential magnitude (red, -667 kJ mol^{-1}) to a low potential magnitude (deep blue, -509 kJ mol^{-1}).

Table S5. Electrostatic potential values at various points on the $[PuCl_3(NO_3)_3]^{2-}$ anion. The atom labels correspond to those depicted in Figure S13.

Coaxial to the bond axis	**Potential in kJ mol-1**
Pu-Cl13	-615
Pu - Cl14	-612
Pu - Cl15	-617
Perpendicular to the bond axis	
Pu-Cl13	-669
Pu - Cl14	-684
Pu - Cl15	-675
Coaxial to the bond axis	
O6	-559
O9	-552
O12	-557
Perpendicular to the bond axis	
O6	-601
O9	-613
O12	-632
Regions between the Cl ligands	
	-734
	-735
	-725
NCI Acceptor Regions	
Cl13 (accepts N4-H4 ··· Cl3)	-672

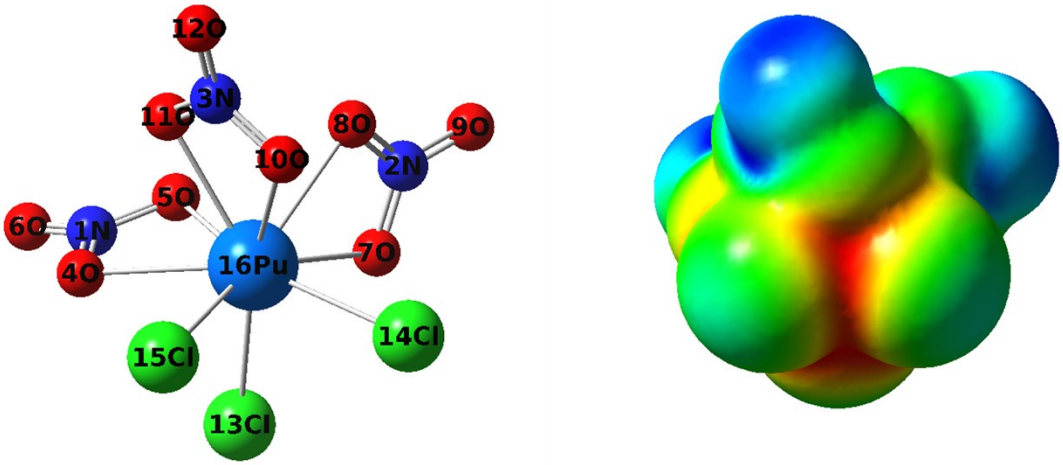

Figure S13. The electrostatic potential of the $[PuCl_3(NO_3)_3]^{2-}$ anion from **2** is mapped on an 0.001au isodensity surface. The color scale represents a gradient from high potential magnitude (red, -740 kJ mol^{-1}) to a low potential magnitude (deep blue, -522 kJ mol^{-1}).

Table S6. Electrostatic potential values at various points on the $[PuCl_4(NO_3)_2]^{2-}$ anion. The atom labels correspond to those depicted in Figure S14.

Coaxial to the bond axis	Potential in kJ mol-1
Pu - Cl9	-604
Pu - Cl10	-606
Pu - Cl11	-602
Pu - Cl12	-603
Perpendicular to the bond axis	
Pu - Cl9	-685
Pu - Cl10	-654
Pu - Cl11	-642
Pu - Cl12	-647
Between the Cl Ligands	
	-720
	-718
	-712
	-710
NCI Acceptor Regions	
Cl9 (accepts N4-HN2 ··· Cl4)	-644 (or -717)
Between Cl10 and Cl11 (accepts N3-HN1 ··· Cl2/Cl3)	-716
O6 (accepts N3-HN1 ··· O6)	-655
O5 (accepts C3-I1 ··· O5)	-665

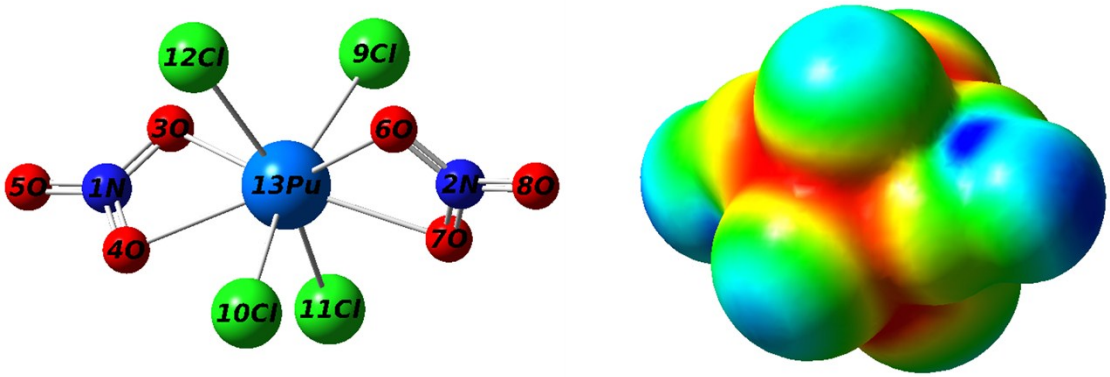

Figure S14. The electrostatic potential of the $[PuCl_4(NO_3)_2]^{2-}$ anion from **3** is mapped on an 0.001au isodensity surface. The color scale represents a gradient from high potential magnitude (red, -722 kJ mol^{-1}) to a low potential magnitude (deep blue, -570 kJ mol^{-1}).

Table S7. Electrostatic potential values at various points on the $[PuO_2Cl_3(NO_3)]^{2-}$ anion. The atom labels correspond to those depicted in Figure S15.

Coaxial to the bond axis	**Potential in kJ mol-1**
Pu – Cl4	-658
Pu – Cl8	-666
Pu – Cl9	-652
Perpendicular to the bond axis	
Pu – Cl4	-724
Pu – Cl8	-714 (Side near Cl4) -717 (Side near NO_3)
Pu – Cl9	-723 (Side near Cl4) -709 (Side near NO3)
Coaxial to the bond axis	
Pu = $O2_{yl}$	-655
Pu = $O3_{yl}$	-656
Between the Cl Ligands	
	-791
	-796
NCI Acceptor Regions	
Between Cl4 and Cl9 (accepts N2-H2a ··· Cl3/Cl2)	-786
Between Cl8 and O5 (accepts N3-H3 ··· O3/Cl1)	-756

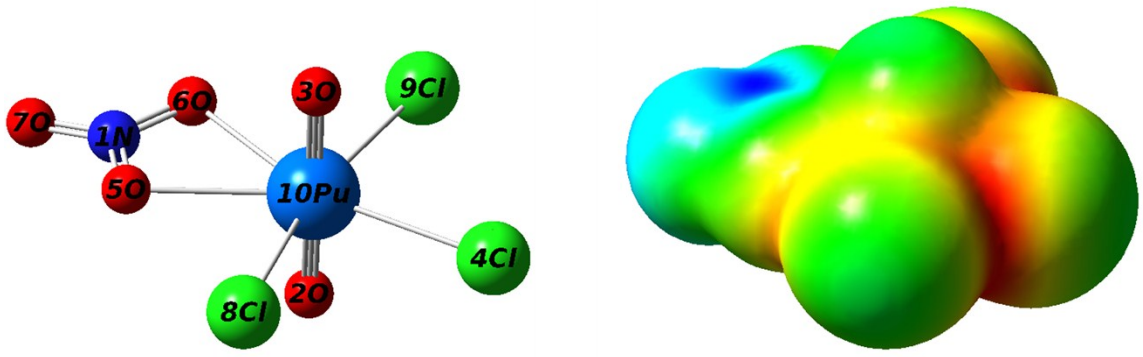

Figure S15. The electrostatic potential of the $[PuO_2Cl_3(NO_3)]^{2-}$ anion from **4** is mapped on an 0.001au isodensity surface. The color scale represents a gradient from high potential magnitude (red, -793 kJ mol^{-1}) to a low potential magnitude (deep blue, -551 kJ mol^{-1}).

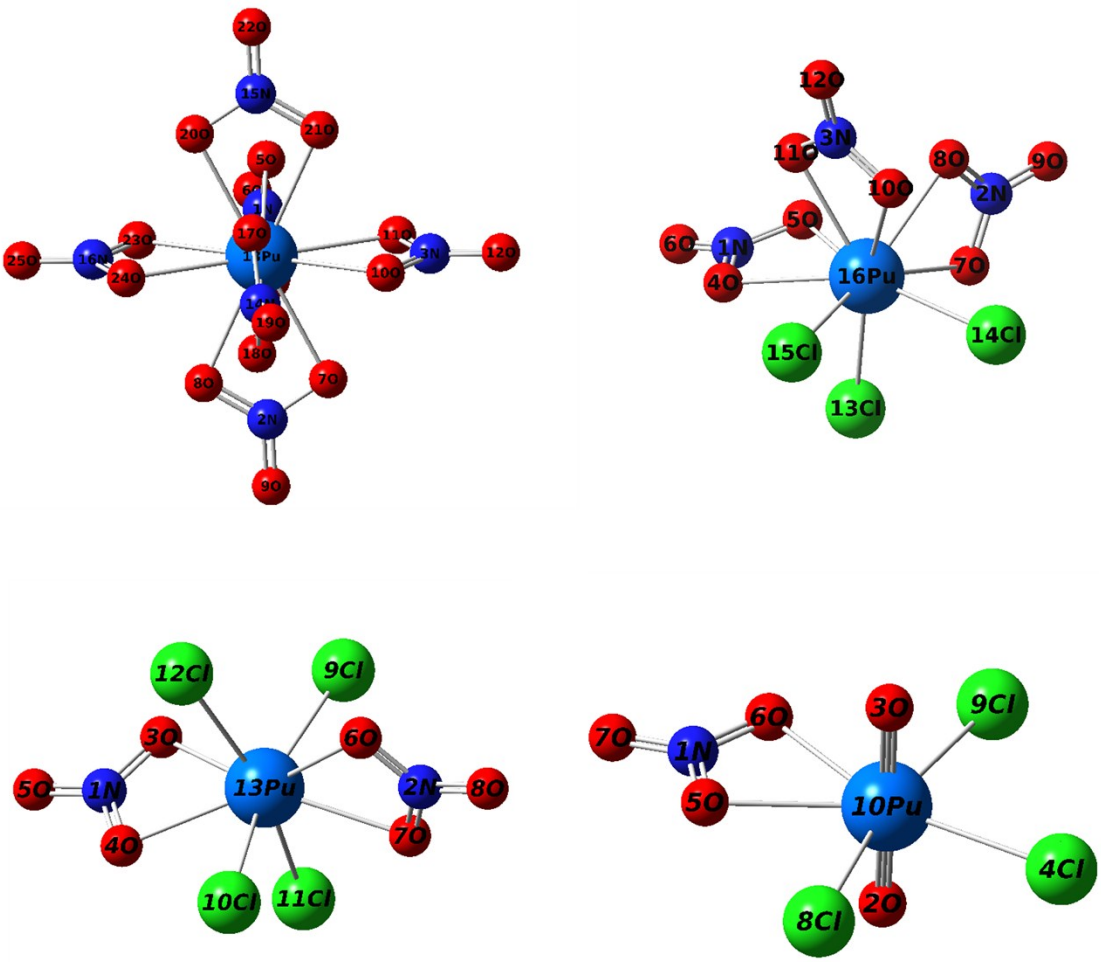

Figure S16. The coordination geometry of each molecular anion was taken from the crystallographic data and was not optimized prior to the QTAIM and NLMO analyses. The atom labels on each anion correspond to the values in Tables S8

Quantum Theory of Atoms in Molecules Analysis (QTAIM)

Table S8. Topological parameters of electron density. All the electron density (ρ), its Laplacian ($\nabla^2\rho$), local kinetic energy density (G), potential energy density (V) and electronic energy density (H) parameters are in 10^3 au whereas the ellipticity (ε) and delocalization index (δ) are dimensionless.

Atoms	ρ	$\nabla^2\rho$	ε	$\delta(A,B)$	H_{BCP}	V_{BCP}	G_{BCP}	$\lvert V_{BCP}\rvert/G_{BCP}$
$[Pu(NO_3)_6]^{2-}$								
O10 - Pu13	0.05185	0.18919	0.06084	0.2567	-0.0050	-0.0573	0.0523	1.0960
O11 - Pu13	0.04863	0.17906	0.05524	0.2438	-0.0041	-0.0529	0.0488	1.0830
O4 - Pu13	0.05242	0.19005	0.07042	0.2620	-0.0052	-0.0579	0.0527	1.0989
O5 - Pu13	0.04946	0.18222	0.05948	0.2466	-0.0043	-0.0541	0.0498	1.0856
O7 - Pu13	0.05285	0.19044	0.06920	0.2650	-0.0054	-0.0584	0.0530	1.1016
O8 - Pu13	0.04940	0.18298	0.05581	0.2446	-0.0042	-0.0542	0.0499	1.0841
$[PuCl_3(NO_3)_3]^{2-}$								
O10 - Pu16	0.04934	0.18465	0.04851	0.2481	-0.0041	-0.0544	0.0503	1.0820
O11 - Pu16	0.05534	0.20375	0.08647	0.2749	-0.0060	-0.0630	0.0570	1.1062
O4 - Pu16	0.05293	0.19416	0.05100	0.2673	-0.0053	-0.0591	0.0538	1.0983
O5 - Pu16	0.05516	0.20371	0.08771	0.2708	-0.0060	-0.0629	0.0569	1.1053
O7 - Pu16	0.05163	0.19176	0.06607	0.2582	-0.0048	-0.0576	0.0528	1.0918
O8 - Pu16	0.05511	0.20442	0.08172	0.2747	-0.0059	-0.0630	0.0570	1.1041
Cl13 - Pu16	0.06723	0.15278	0.08008	0.5664	-0.0152	-0.0685	0.0534	1.2841
Cl14 - Pu16	0.06894	0.15814	0.08555	0.5792	-0.0159	-0.0714	0.0555	1.2873
Cl15 - Pu16	0.06565	0.14959	0.04868	0.5593	-0.0145	-0.0663	0.0519	1.2790
$[PuCl_4(NO_3)_2]^{2-}$								
O3 - Pu13	0.05620	0.20717	0.04796	0.2580	-0.0067	-0.0651	0.0584	1.1138
O4 - Pu13	0.05233	0.19389	0.03083	0.2667	-0.0049	-0.0582	0.0533	1.0914
O6 - Pu13	0.05991	0.21644	0.11781	0.2702	-0.0079	-0.0699	0.0620	1.1273
O7 - Pu13	0.05772	0.21040	0.08462	0.2619	-0.0072	-0.0671	0.0598	1.1210
Cl10 - Pu13	0.06724	0.15074	0.01386	0.5965	-0.0150	-0.0676	0.0526	1.2841
Cl11 - Pu13	0.06637	0.14474	0.06699	0.5942	-0.0146	-0.0653	0.0508	1.2871
Cl12 - Pu13	0.06617	0.14184	0.10951	0.5971	-0.0145	-0.0644	0.0499	1.2896
Cl9 - Pu13	0.06817	0.15390	0.03460	0.5957	-0.0155	-0.0695	0.0540	1.2876
$[PuO_2Cl_3(NO_3)]^{2-}$								
O5 - Pu10	0.04841	0.18645	0.29027	0.2344	-0.0035	-0.0535	0.0501	1.0691
O6 - Pu10	0.04329	0.16907	0.26758	0.2140	-0.0022	-0.0467	0.0445	1.0494
O2 = Pu10	0.32794	0.35255	0.00542	1.9763	-0.2984	-0.6850	0.3866	1.7720
O3 = Pu10	0.31845	0.35894	0.00592	1.9637	-0.2810	-0.6518	0.3707	1.7580
Cl4 - Pu10	0.05371	0.13148	0.16020	0.4813	-0.0088	-0.0504	0.0416	1.2105
Cl8 - Pu10	0.05716	0.13594	0.16676	0.4973	-0.0101	-0.0542	0.0441	1.2288
Cl9 - Pu10	0.05829	0.14056	0.15335	0.5058	-0.0105	-0.0561	0.0456	1.2295

Natural Localized Molecular Orbital (NLMO) Analysis

These Pu systems are open shell and as such, the alpha and beta electron spins were considered in the natural localized molecular orbital analyses. The results compiled in Tables S9 and S10 reflect only the alpha spins, yet each consideration is reported in full in the following section. The orbital contributions that contribute greater than 1% (relative to the total) are included in Table S9 whereas all others have been omitted.

Table S9. Select NLMO data that describes the hybrid atomic orbitals and their contribution to the Pu-NO_3 bonds in **1-4**.

Bond	O - HAO	N - HAO	Pu - HAO
1: Pu – O4	89% - (s 32%, p 67%)	1% - (s 3%, p 93%, d 4%)	9% - (s 10%, d 37%, f 52%)
1: Pu – O5	90% - (s 39%, p 61%)	1% - (s 2%, p 94%, d 4%)	8% - (s 12%, d 41%, f 47%)
2: Pu – O4	89% - (s 30%, p 69%)	1% - (s 3%, p 93%, d 4%)	8% - (s 12%, d 41%, f 47%)
2: Pu – O5	90% - (s 34%, p 66%)	1% - (s 4%, p 92%, d 4%)	9% - (s 13%, d 48%, f 39%)
3: Pu – O3	91% - (s 33%, p 67%)	1% - (s 2%, p 93%, d 4 %)	6% - (s 18%, d 61%, f 21%)
3: Pu – O4	89% - (s 29%, p 71%)	1% - (s 2%, p 94%, d 4%)	8% - (s 12%, d 46%, f 43%)
4: Pu – O5	90% - (s 25%, p 75%)	1% - (s 3%, p 92%, d 5%)	7% - (s 14%, d 51%, f 35%)
4: Pu – O6	90% - (s 24%, p 76%)	1% - (s 3%, p 92%, d 5%)	7% - (s 15%, d 50%, f 35%)

Table S10. Select NLMO data that describes the hybrid atomic orbitals and their contribution to the Pu-Cl and Pu=O_{yl} bonds in **1-4**.

Bond	Cl – HAO	Pu - HAO
2: Pu – Cl13	BD1: 86% - (s 37%, p 63%)	14% - (s 17%, d 53%, f 30%)
2: Pu – Cl14	BD1: 87% - (s 40%, p 60%)	13% - (s 19%, d 57%, f 25%)
2: Pu – C14	BD2: 89% - (s 27%, p 73%)	11% - (s 14%, d 52%, f 33%)
3: Pu – Cl9	BD1: 84% - (3s 30%, p 69%)	16% - (s 15%, d 41%, f 44%)
4: Pu – Cl4	BD1: 85% - (s 28%, p 72%)	14% - (s 18%, d 47%, f 35%)
***4**: Pu – $O2_{'oxo'}$	BD1: 66% - (s 4%, p 96%)	33% - (d 20%, f 79%)
	BD2: 58% - (s 14%, p 85%)	41% - (d 10%, f 89%)
	BD3: 70% - (p 100%)	29% - (d 28%, f 72%)

Results corresponding to the $[Pu(NO_3)_6]^{2-}$ anion:

Pu –$O_{(nitrate)}$ bonding

79. (1.00000) 95.7491% BD (1) O4 – Pu13
9.061% Pu 13 s(10.50%)p 0.01(0.11%)d 3.53(37.05%)f 4.98(52.33%)
1.084% N 1 s(3.02%)p30.64(92.56%)d 1.38(4.15%)
88.742% O 4 s(32.46%)p 2.08(67.42%)

75. (1.00000) 96.4258% BD (1) O4 – Pu13
7.787% Pu 13 s(12.21%)p 0.01(0.11%)d 3.33(40.69%)f 3.85(46.97%)
1.037% N 1 s(2.20%)p42.53(93.57%)d 1.81(3.98%)
90.196% O 4 s(38.84%)p 1.57(61.05%)

80. (1.00000) 95.5698% BD (1) O5 – Pu13
8.705% Pu 13 s(11.09%)p 0.01(0.11%)d 3.46(38.33%)f 4.55(50.46%)
1.189% N 1 s(2.73%)p34.03(92.92%)d 1.50(4.09%)
88.902% O 5 s(31.40%)p 2.18(68.47%)

76. (1.00000) 96.2236% BD (1) O5 – Pu13
7.548% Pu 13 s(12.93%)p 0.01(0.11%)d 3.21(41.51%)f 3.52(45.44%)
1.136% N 1 s(2.02%)p46.49(93.83%)d 1.94(3.91%)
90.255% O 5 s(37.23%)p 1.68(62.65%)

82. (1.00000) 95.8527% BD (1) O7 – Pu13
9.116% Pu 13 s(10.43%)p 0.01(0.11%)d 3.56(37.13%)f 5.01(52.31%)
1.036% N 2 s(3.21%)p28.74(92.24%)d 1.33(4.27%)
88.776% O 7 s(32.54%)p 2.07(67.34%)

78. (1.00000) 96.5301% BD (1) O7 – Pu13
7.859% Pu 13 s(12.26%)p 0.01(0.11%)d 3.32(40.71%)f 3.83(46.90%)
0.991% N 2 s(2.35%)p39.70(93.31%)d 1.74(4.08%)
90.209% O 7 s(39.11%)p 1.55(60.78%)

83. (1.00000) 95.6323% BD (1) O8 – Pu13
8.658% Pu 13 s(11.06%)p 0.01(0.12%)d 3.46(38.31%)f 4.57(50.50%)
1.172% N 2 s(2.76%)p33.64(92.87%)d 1.49(4.11%)
88.972% O 8 s(31.35%)p 2.19(68.52%)

79. (1.00000) 96.3009% BD (1) O8 – Pu13
7.532% Pu 13 s(12.82%)p 0.01(0.11%)d 3.22(41.31%)f 3.57(45.75%)
1.121% N 2 s(2.00%)p47.00(93.82%)d 1.97(3.93%)
90.297% O 8 s(37.06%)p 1.70(62.82%)

85. (1.00000) 95.7138% BD (1) O10 – Pu13
8.906% Pu 13 s(10.66%)p 0.01(0.11%)d 3.50(37.30%)f 4.87(51.92%)
1.120% N 3 s(2.28%)p40.82(93.19%)d 1.87(4.26%)
88.806% O 10 s(31.07%)p 2.21(68.80%)

81. (1.00000) 96.4004% BD (1) O10 – Pu13
7.707% Pu 13 s(12.34%)p 0.01(0.11%)d 3.30(40.69%)f 3.80(46.84%)
1.074% N 3 s(1.65%)p57.07(94.00%)d 2.49(4.10%)
90.181% O 10 s(36.92%)p 1.71(62.96%)

86. (1.00000) 95.5057% BD (1) O11 – Pu13
8.678% Pu 13 s(11.18%)p 0.01(0.12%)d 3.46(38.62%)f 4.48(50.08%)
1.212% N 3 s(2.23%)p41.80(93.34%)d 1.87(4.17%)
88.883% O 11 s(30.27%)p 2.30(69.60%)

82. (1.00000) 96.1407% BD (1) O 11-Pu 13
7.511% Pu 13 s(13.07%)p 0.01(0.11%)d 3.18(41.63%)f 3.46(45.17%)
1.163% N 3 s(1.60%)p58.68(94.14%)d 2.50(4.02%)
90.231% O 11 s(35.80%)p 1.79(64.08%)

87. (1.00000) 95.7491% BD (1) Pu13 – O17
9.061% Pu 13 s(10.50%)p 0.01(0.11%)d 3.53(37.05%)f 4.98(52.33%)
1.084% N 14 s(3.02%)p30.64(92.56%)d 1.38(4.15%)
88.742% O 17 s(32.46%)p 2.08(67.42%)

83. (1.00000) 96.4258% BD (1)Pu13 – O17
7.787% Pu 13 s(12.21%)p 0.01(0.11%)d 3.33(40.69%)f 3.85(46.97%)
1.037% N 14 s(2.20%)p42.53(93.57%)d 1.81(3.98%)
90.196% O 17 s(38.84%)p 1.57(61.05%)

88. (1.00000) 95.5698% BD (1) Pu13 – O18
8.705% Pu 13 s(11.09%)p 0.01(0.11%)d 3.46(38.33%)f 4.55(50.46%)
1.189% N 14 s(2.73%)p34.03(92.92%)d 1.50(4.09%)
88.902% O 18 s(31.40%)p 2.18(68.47%)

84. (1.00000) 96.2236% BD (1) Pu13 – O18
7.548% Pu 13 s(12.93%)p 0.01(0.11%)d 3.21(41.51%)f 3.52(45.44%)
1.136% N 14 s(2.02%)p46.49(93.83%)d 1.94(3.91%)
90.255% O 18 s(37.23%)p 1.68(62.65%)

89. (1.00000) 95.8527% BD (1) Pu13 – O20
9.116% Pu 13 s(10.43%)p 0.01(0.11%)d 3.56(37.13%)f 5.01(52.31%)
1.036% N 15 s(3.21%)p28.74(92.24%)d 1.33(4.27%)
88.776% O 20 s(32.54%)p 2.07(67.34%)

85. (1.00000) 96.5301% BD (1) Pu13 – O20
7.859% Pu 13 s(12.26%)p 0.01(0.11%)d 3.32(40.71%)f 3.83(46.90%)
90.209% O 20 s(39.11%)p 1.55(60.78%)
0.991% N 15 s(2.35%)p39.70(93.31%)d 1.74(4.08%)

90. (1.00000) 95.6323% BD (1) Pu 3 – O21

8.658% Pu 13 s(11.06%)p 0.01(0.12%)d 3.46(38.31%)f 4.57(50.50%)
1.172% N 15 s(2.76%)p33.64(92.87%)d 1.49(4.11%)
88.972% O 21 s(31.35%)p 2.19(68.52%)

86. (1.00000) 96.3009% BD (1) Pu13 – O21
7.532% Pu 13 s(12.82%)p 0.01(0.11%)d 3.22(41.31%)f 3.57(45.75%)
1.121% N 15 s(2.00%)p47.00(93.82%)d 1.97(3.93%)
90.297% O 21 s(37.06%)p 1.70(62.82%)

91. (1.00000) 95.7138% BD (1) Pu13 – O23
8.906% Pu 13 s(10.66%)p 0.01(0.11%)d 3.50(37.30%)f 4.87(51.92%)
1.120% N 16 s(2.28%)p40.82(93.19%)d 1.87(4.26%)
88.806% O 23 s(31.07%)p 2.21(68.80%)

87. (1.00000) 96.4004% BD (1) Pu13 – O23
7.707% Pu 13 s(12.34%)p 0.01(0.11%)d 3.30(40.69%)f 3.80(46.84%)
1.074% N 16 s(1.65%)p57.07(94.00%)d 2.49(4.10%)
90.181% O 23 s(36.92%)p 1.71(62.96%)

92. (1.00000) 95.5057% BD (1) Pu13 – O24
8.678% Pu 13 s(11.18%)p 0.01(0.12%)d 3.46(38.62%)f 4.48(50.08%)
1.212% N 16 s(2.23%)p41.80(93.34%)d 1.87(4.17%)
88.883% O 24 s(30.27%)p 2.30(69.60%)

88. (1.00000) 96.1407% BD (1) Pu13 – O24
7.511% Pu 13 s(13.07%)p 0.01(0.11%)d 3.18(41.63%)f 3.46(45.17%)
1.163% N 16 s(1.60%)p58.68(94.14%)d 2.50(4.02%)
90.231% O 24 s(35.80%)p 1.79(64.08%)

NLMO Results from the $[PuCl_3(NO_3)_3]^{2-}$ Anion

Pu – Cl Bond

87. (1.00000) 98.2254% BD (1) Cl13 – Pu16
85.787% Cl 13 s(36.85%)p 1.71(62.87%)
13.951% Pu 16 s(17.15%)p 0.01(0.09%)d 3.09(53.04%)f 1.73(29.72%)

82. (1.00000) 98.3675% BD (1) Cl13 – Pu16
86.168% Cl 13 s(44.16%)p 1.26(55.55%)
13.648% Pu 16 s(18.51%)p 0.00(0.06%)d 2.74(50.74%)f 1.66(30.68%)

88. (1.00000) 98.0902% BD (1) Cl14 – Pu16
86.803% Cl 14 s(39.60%)p 1.52(60.14%)
12.944% Pu 16 s(18.52%)p 0.00(0.09%)d 3.06(56.64%)f 1.34(24.74%)

83. (1.00000) 99.0838% BD (1) Cl14 – Pu16

90.537% Cl 14 s(16.08%)p 5.21(83.78%)
9.307% Pu 16 s(10.55%)p 0.01(0.13%)d 5.02(52.93%)f 3.45(36.38%)

84. (1.00000) 98.3322% BD (2) Cl14 – Pu16
89.288% Cl 14 s(27.05%)p 2.69(72.75%)
10.577% Pu 16 s(14.54%)p 0.01(0.10%)d 3.61(52.47%)f 2.26(32.87%)

89. (1.00000) 98.0971% BD (1) Cl15 – Pu16
86.798% Cl 15 s(39.14%)p 1.55(60.61%)
12.926% Pu 16 s(18.68%)p 0.01(0.10%)d 3.07(57.29%)f 1.28(23.92%)

85. (1.00000) 98.2876% BD (1) Cl15 – Pu16
86.294% Cl 15 s(43.83%)p 1.28(55.90%)
13.507% Pu 16 s(19.18%)p 0.00(0.07%)d 2.65(50.75%)f 1.56(29.99%)

Pu – $O_{(nitrate)}$ Bond

79. (1.00000) 95.9240% BD (1) O4 – Pu16
1.144% N 1 s(2.85%)p32.58(92.71%)d 1.47(4.19%)
89.268% O 4 s(30.46%)p 2.28(69.41%)
8.480% Pu 16 s(12.17%)p 0.01(0.12%)d 3.35(40.76%)f 3.86(46.94%)

74. (1.00000) 96.6323% BD (1) O4 – Pu16
1.111% N 1 s(2.37%)p39.38(93.36%)d 1.70(4.03%)
90.700% O 4 s(35.76%)p 1.79(64.12%)
7.179% Pu 16 s(13.56%)p 0.01(0.12%)d 3.34(45.23%)f 3.03(41.08%)

80. (1.00000) 96.3197% BD (1) O5 – Pu16
1.080% N 1 s(3.96%)p23.20(91.82%)d 1.00(3.96%)
89.709% O 5 s(33.74%)p 1.96(66.15%)
8.121% Pu 16 s(12.85%)p 0.01(0.10%)d 3.75(48.22%)f 3.02(38.83%)

75. (1.00000) 96.6221% BD (1) O5 – Pu16
1.052% N 1 s(2.67%)p34.89(93.18%)d 1.46(3.90%)
90.747% O 5 s(37.69%)p 1.65(62.20%)
7.211% Pu 16 s(13.79%)p 0.01(0.09%)d 3.48(47.99%)f 2.76(38.12%)

82. (1.00000) 95.9096% BD (1) O7 – Pu16
1.160% N 2 s(3.37%)p27.39(92.25%)d 1.23(4.13%)
89.484% O 7 s(31.25%)p 2.20(68.62%)
8.193% Pu 16 s(12.44%)p 0.01(0.12%)d 3.29(40.89%)f 3.74(46.53%)

77. (1.00000) 96.5163% BD (1) O7 – Pu16
1.129% N 2 s(2.49%)p37.42(93.28%)d 1.60(3.98%)
90.812% O 7 s(36.06%)p 1.77(63.82%)
7.045% Pu 16 s(14.03%)p 0.01(0.12%)d 3.25(45.62%)f 2.87(40.22%)

83. (1.00000) 96.5437% BD (1) O8 – Pu16

1.020% N 2 s(4.18%)p21.86(91.48%)d 0.97(4.08%)
89.676% O 8 s(34.42%)p 1.90(65.47%)
8.271% Pu 16 s(13.19%)p 0.01(0.10%)d 3.61(47.66%)f 2.96(39.04%)

78. (1.00000) 96.6961% BD (1) O8 – Pu16
90.753% O 8 s(38.94%)p 1.57(60.95%)
7.297% Pu 16 s(14.42%)p 0.01(0.10%)d 3.46(49.87%)f 2.47(35.60%)

85. (1.00000) 95.9670% BD (1) O10 – Pu16
1.210% N 3 s(3.13%)p29.51(92.48%)d 1.31(4.12%)
89.540% O 10 s(29.88%)p 2.34(69.99%)
8.060% Pu 16 s(12.52%)p 0.01(0.13%)d 3.17(39.69%)f 3.81(47.65%)

80. (1.00000) 96.5712% BD (1) O10 – Pu16
1.167% N 3 s(2.40%)p38.83(93.36%)d 1.66(3.98%)f 0.10(0.25%)
90.865% O 10 s(34.92%)p 1.86(64.96%)
6.929% Pu 16 s(13.93%)p 0.01(0.12%)d 3.22(44.91%)f 2.95(41.04%)

86. (1.00000) 96.7129% BD (1) O11 – Pu16
1.009% N 3 s(4.32%)p21.15(91.31%)d 0.95(4.11%)
89.597% O 11 s(34.43%)p 1.90(65.46%)
8.362% Pu 16 s(12.79%)p 0.01(0.10%)d 3.83(49.00%)f 2.98(38.10%)

81. (1.00000) 96.7476% BD (1) O11 – Pu16
90.742% O 11 s(38.73%)p 1.58(61.16%)
7.316% Pu 16 s(14.32%)p 0.01(0.10%)d 3.38(48.47%)f 2.59(37.10%)
0.983% N 3 s(2.95%)p31.44(92.79%)d 1.36(4.00%)

NLMO Results from the $[PuCl_4(NO_3)_2]^{2-}$ Anion

Pu – Cl Bonding

79. (1.00000) 98.9884% BD (1) Cl9 – Pu13
83.646% Cl 9 s(30.49%)p 2.27(69.17%)
16.189% Pu 13 s(15.05%)p 0.01(0.09%)d 2.72(40.87%)f 2.92(43.97%)

72. (1.00000) 99.2373% BD (1) Cl9 - Pu13
94.169% Cl 9 s(0.97%)p99.99(98.96%)
5.648% Pu 13 s(0.54%)p 0.44(0.24%)d99.99(55.99%)f80.07(43.23%)

73. (1.00000) 97.2450% BD (2) Cl9 – Pu13
87.542% Cl 9 s(41.42%)p 1.41(58.32%)
12.264% Pu 13 s(19.11%)p 0.00(0.05%)d 2.70(51.62%)f 1.53(29.21%)

80. (1.00000) 98.7561% BD (1) Cl10 – Pu13

83.076% Cl 10 s(30.43%)p 2.27(69.22%)
16.755% Pu 13 s(15.09%)p 0.01(0.09%)d 2.64(39.82%)f 2.98(45.00%)

74. (1.00000) 99.2555% BD (1) Cl10 – Pu13
94.198% Cl 10 s(1.93%)p50.88(98.00%)
5.598% Pu 13 s(1.29%)p 0.18(0.23%)d42.64(54.79%)f33.99(43.69%)

75. (1.00000) 97.1533% BD (2) Cl10 – Pu13
87.601% Cl 10 s(41.50%)p 1.40(58.25%)
12.202% Pu 13 s(19.36%)p 0.00(0.04%)d 2.69(51.98%)f 1.48(28.61%)

81. (1.00000) 98.7342% BD (1) Cl11 – Pu13
83.606% Cl 11 s(29.61%)p 2.37(70.07%)
16.234% Pu 13 s(15.02%)p 0.01(0.11%)d 2.69(40.42%)f 2.96(44.44%)

76. (1.00000) 99.3094% BD (1) Cl11 - Pu13
94.386% Cl 11 s(0.96%)p99.99(98.97%)
5.436% Pu 13 s(0.75%)p 0.29(0.22%)d73.55(55.12%)f58.59(43.90%)

77. (1.00000) 97.0659% BD (2) Cl11 - Pu 3
88.060% Cl 11 s(38.49%)p 1.59(61.28%)
11.746% Pu 13 s(18.77%)p 0.00(0.06%)d 2.82(52.85%)f 1.51(28.31%)

82. (1.00000) 98.8209% BD (1) Cl12 - Pu13
86.861% Cl 12 s(14.71%)p 5.78(85.07%)
12.959% Pu 13 s(10.28%)p 0.01(0.13%)d 4.13(42.48%)f 4.58(47.10%)

78. (1.00000) 99.2203% BD (1) Cl12 – Pu13
94.063% Cl 12 s(2.88%)p33.76(97.05%)
5.742% Pu 13 s(2.06%)p 0.10(0.20%)d26.20(53.87%)f21.33(43.86%)

79. (1.00000) 97.1178% BD (2) Cl12 – Pu13
88.540% Cl 12 s(35.60%)p 1.80(64.19%)
11.259% Pu 13 s(18.39%)p 0.00(0.06%)d 2.89(53.16%)f 1.54(28.38%)

83. (1.00000) 98.2283% BD (2) Cl12 – Pu13
88.538% Cl 12 s(13.35%)p 6.48(86.48%)
11.295% Pu 13 s(10.34%)p 0.01(0.12%)d 4.68(48.35%)f 3.98(41.18%)

Pu-$O_{(nitrate)}$ Bonding

74. (1.00000) 96.0770% BD (1) O3 – Pu13
1.273% N 1 s(2.47%)p37.68(93.01%)d 1.72(4.26%)
91.440% O 3 s(32.60%)p 2.06(67.28%)
6.071% Pu 13 s(17.53%)p 0.01(0.14%)d 3.49(61.15%)f 1.21(21.17%)

67. (1.00000) 95.6844% BD (1) O3 - Pu13

1.232% N 1 s(1.70%)p55.16(93.82%)d 2.48(4.22%)
90.750% O 3 s(34.43%)p 1.90(65.45%)
6.914% Pu 13 s(15.05%)p 0.01(0.08%)d 3.19(47.99%)f 2.45(36.86%)

75. (1.00000) 96.2316% BD (1) O4 – Pu13
1.214% N 1 s(1.95%)p48.04(93.51%)d 2.20(4.28%)
89.425% O 4 s(28.71%)p 2.48(71.16%)
8.177% Pu 13 s(12.52%)p 0.01(0.10%)d 3.56(44.56%)f 3.42(42.81%)

68. (1.00000) 95.7432% BD (1) O4 – Pu13
1.165% N 1 s(1.80%)p52.12(93.85%)d 2.27(4.09%)
90.912% O 4 s(34.08%)p 1.93(65.80%)
6.849% Pu 13 s(14.56%)p 0.01(0.09%)d 3.36(48.87%)f 2.50(36.47%)

77. (1.00000) 96.2517% BD (1) O6 – Pu13
1.319% N 2 s(1.61%)p58.15(93.88%)d 2.63(4.25%)
91.087% O 6 s(30.97%)p 2.22(68.89%)
6.316% Pu 13 s(16.95%)p 0.01(0.14%)d 3.51(59.44%)f 1.38(23.44%)

70. (1.00000) 95.5637% BD (1) O6 – Pu13
1.262% N 2 s(1.49%)p63.13(94.11%)d 2.78(4.15%)
90.527% O 6 s(34.03%)p 1.93(65.84%)
7.075% Pu 13 s(14.77%)p 0.01(0.09%)d 3.23(47.68%)f 2.53(37.44%)

78. (1.00000) 96.0732% BD (1) O7 - Pu13
1.269% N 2 s(1.76%)p53.24(93.58%)d 2.49(4.39%)
91.311% O 7 s(31.05%)p 2.22(68.82%)
6.121% Pu 13 s(16.96%)p 0.01(0.14%)d 3.61(61.29%)f 1.27(21.59%)

71. (1.00000) 95.5797% BD (1) O7 – Pu13
1.222% N 2 s(1.57%)p59.93(93.85%)d 2.76(4.32%)
90.607% O 7 s(33.52%)p 1.98(66.35%)
7.037% Pu 13 s(14.62%)p 0.01(0.08%)d 3.28(47.97%)f 2.55(37.30%)

NLMO Results from the $[PuO_2Cl_3(NO_3)]^{2-}$ Anion

Pu = O_{yl} Bonding

57. (1.00000) 98.1457% BD (1) O 2 - Pu10 'yl'
66.398% O 2 s(3.55%)p27.05(96.02%)
33.216% Pu 10 s(0.02%)p 8.79(0.17%)d99.99(20.46%)f99.99(79.32%)

55. (1.00000) 98.6965% BD (1) O 2-Pu 10 'yl'
81.415% O 2 s(0.00%)p 1.00(99.67%)
18.409% Pu 10 s(0.00%)p 1.00(0.05%)d99.99(33.90%)f99.99(65.99%)

58. (1.00000) 97.5849% BD (2) O 2 - Pu 10 'yl'

58.046% O 2 s(14.42%)p 5.90(85.08%)
41.452% Pu 10 s(0.04%)p 5.33(0.23%)d99.99(10.27%)f99.99(89.44%)

56. (1.00000) 97.7635% BD (2) O 2-Pu 10 'yl'
79.110% O 2 s(3.95%)p24.21(95.69%)
20.373% Pu 10 s(0.07%)p 3.73(0.25%)d99.99(30.32%)f99.99(69.31%)

59. (1.00000) 97.0691% BD (3) O 2-Pu 10 'yl'
70.262% O 2 s(0.00%)p 1.00(99.60%)
29.067% Pu 10 s(0.00%)p 1.00(0.04%)d99.99(28.10%)f99.99(71.82%)

60. (1.00000) 97.0937% BD (1) O 3-Pu 10 'yl'
70.334% O 3 s(0.01%)p 1.00(99.61%))
28.887% Pu 10 s(0.00%)p 1.00(0.04%)d99.99(28.82%)f99.99(71.10%)

57. (1.00000) 98.6545% BD (1) O 3-Pu 10 'yl'
76.216% O 3 s(7.17%)p12.89(92.47%)
23.576% Pu 10 s(0.08%)p 3.33(0.26%)d99.99(21.81%)f99.99(77.82%)

61. (1.00000) 96.6730% BD (2) O 3-Pu 10 'yl'
69.832% O 3 s(0.96%)p99.99(98.65%)
29.043% Pu 10 s(0.01%)p 1.00(0.18%)d99.99(29.68%)f99.99(70.09%)

58. (1.00000) 98.7301% BD (2) O 3-Pu 10 'yl'
81.682% O 3 s(0.00%)p 1.00(99.68%)
18.101% Pu 10 s(0.00%)p 1.00(0.06%)d99.99(34.74%)f99.99(65.14%)

59. (1.00000) 97.3302% BD (3) O 3-Pu 10 'yl'
69.423% O 3 s(14.93%)p 5.67(84.65%)
30.119% Pu 10 s(0.07%)p 5.03(0.37%)d99.99(14.80%)f99.99(84.73%)

Pu - Cl Bonding

62. (1.00000) 97.6307% BD (1)Cl 4-Pu 10
85.225% Cl 4 s(28.17%)p 2.55(71.69%)
14.232% Pu 10 s(18.26%)p 0.01(0.19%)d 2.56(46.84%)f 1.90(34.70%)

60. (1.00000) 98.1079% BD (1)Cl 4-Pu 10
87.182% Cl 4 s(34.08%)p 1.93(65.78%)
12.539% Pu 10 s(20.57%)p 0.01(0.17%)d 2.50(51.43%)f 1.35(27.82%)

67. (1.00000) 97.3052% BD (1)Cl 9-Pu 10
84.610% Cl 9 s(27.93%)p 2.57(71.91%)
14.767% Pu 10 s(17.47%)p 0.01(0.14%)d 2.59(45.22%)f 2.13(37.17%)

65. (1.00000) 97.6047% BD (1)Cl 9-Pu 10

87.028% Cl 9 s(34.85%)p 1.86(65.00%)
12.598% Pu 10 s(19.34%)p 0.01(0.12%)d 2.61(50.41%)f 1.56(30.12%)

66. (1.00000) 97.2768% BD (1)Cl 8-Pu 10
84.431% Cl 8 s(27.03%)p 2.69(72.81%)
14.895% Pu 10 s(16.45%)p 0.01(0.15%)d 2.69(44.23%)f 2.38(39.17%)

64. (1.00000) 97.5642% BD (1)Cl 8-Pu 10
87.020% Cl 8 s(34.15%)p 1.92(65.70%)
12.581% Pu 10 s(18.96%)p 0.01(0.13%)d 2.65(50.24%)f 1.62(30.66%)

Pu – $O_{(nitrate)}$ Bonding

64. (1.00000) 95.8516% BD (1) O 5-Pu 10
1.248% N 1 s(3.13%)p29.37(91.84%)d 1.51(4.72%)
90.032% O 5 s(25.33%)p 2.94(74.55%)
7.286% Pu 10 s(13.78%)p 0.01(0.19%)d 3.68(50.66%)f 2.57(35.36%)

62. (1.00000) 95.9224% BD (1) O 5-Pu 10
1.233% N 1 s(2.99%)p30.75(92.03%)d 1.56(4.67%)
90.904% O 5 s(27.45%)p 2.64(72.43%)
6.575% Pu 10 s(14.84%)p 0.01(0.19%)d 3.48(51.63%)f 2.25(33.33%)

65. (1.00000) 95.8180% BD (1) O 6-Pu 10
1.343% N 1 s(3.05%)p30.17(91.90%)d 1.56(4.75%)
90.377% O 6 s(23.68%)p 3.22(76.20%)
6.818% Pu 10 s(14.78%)p 0.02(0.22%)d 3.40(50.20%)f 2.35(34.78%)

63. (1.00000) 95.8728% BD (1) O 6-Pu 10
1.324% N 1 s(2.87%)p32.04(92.12%)d 1.63(4.70%)
91.206% O 6 s(25.61%)p 2.90(74.27%)
6.139% Pu 10 s(16.14%)p 0.01(0.20%)d 3.15(50.78%)f 2.04(32.87%)

6. Black and White Renderings of Figures 1 – 4 from the Communication

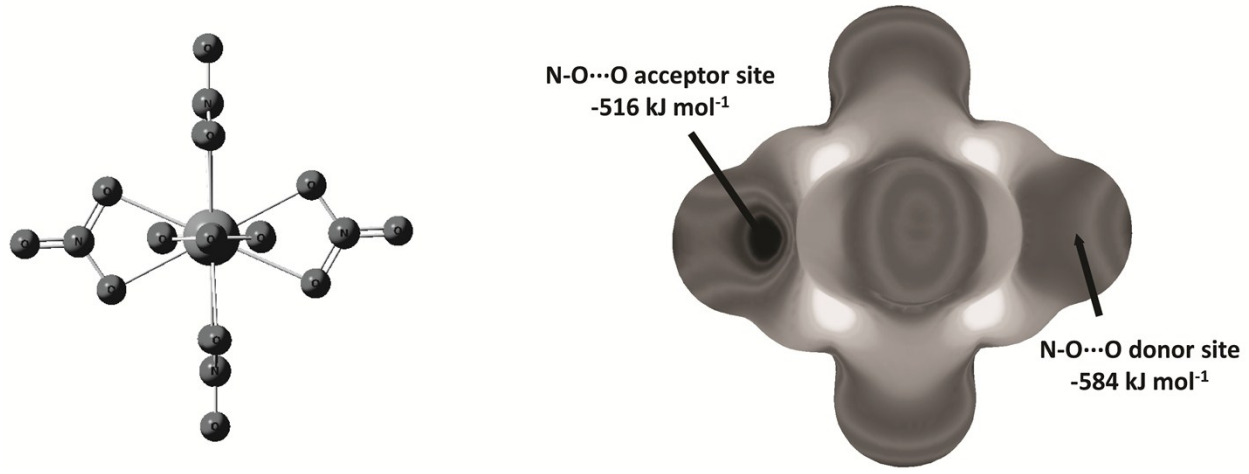

Figure S17. The electrostatic potential of the $[Pu(NO_3)_6]^{2-}$ anion in **1** mapped on an 0.001au isodensity surface. The gradient (white to black) represents a potential of -667 kJ mol^{-1} to -509 kJ mol^{-1}.

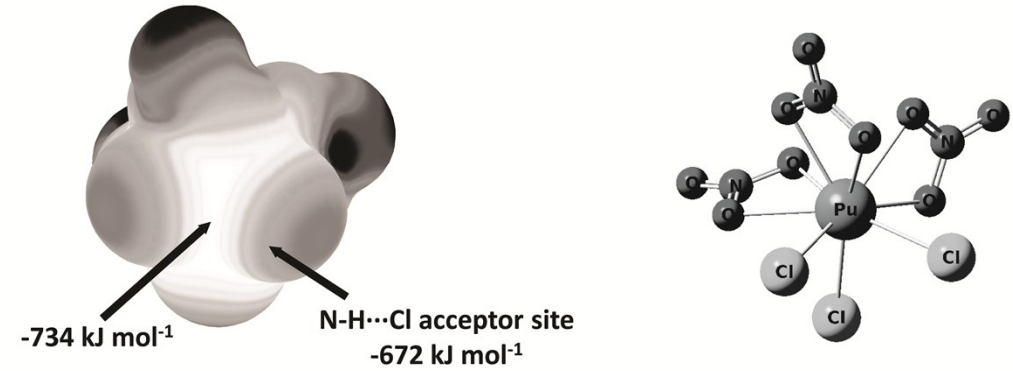

Figure S18. The electrostatic potential of the $[PuCl_3(NO_3)_3]^{2-}$ anion in **2** mapped on an 0.001au isodensity surface. The gradient (white to black) represents a potential of -740 kJ mol^{-1} to -522 kJ mol^{-1}.

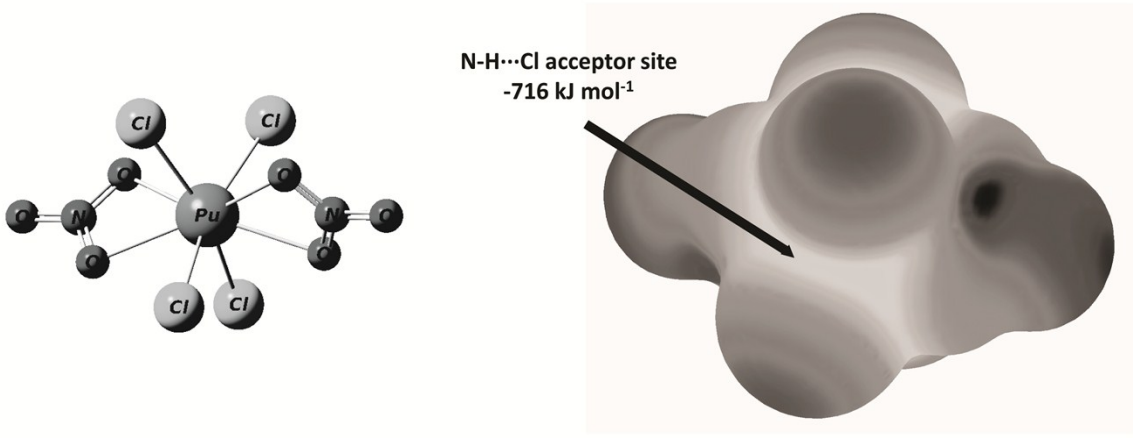

Figure S19. The electrostatic potential of the $[PuCl_4(NO_3)_2]^{2-}$ anion in **3** mapped on an 0.001au isodensity surface. The gradient (white to black) represents a magnitude of -722 kJ mol^{-1} to -570 kJ mol^{-1}.

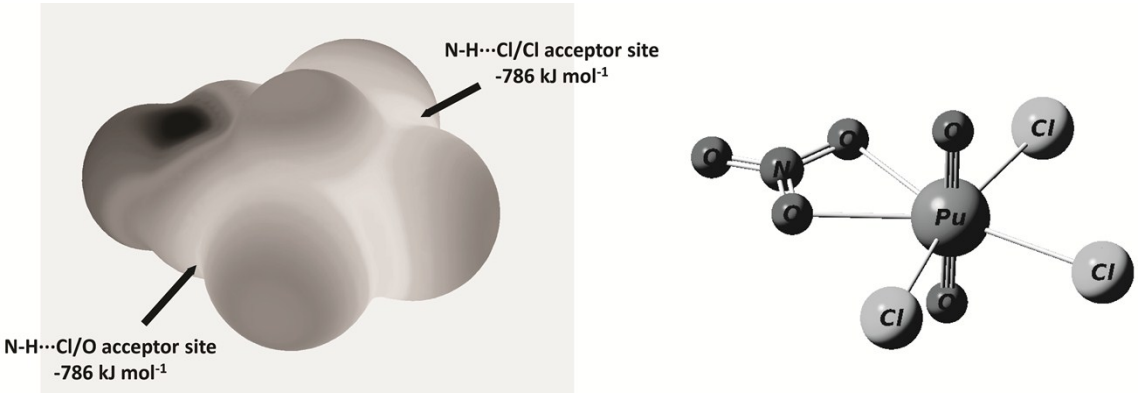

Figure S20. The electrostatic potential of the $[PuO_2Cl_3(NO_3)]^{2-}$ anion in **4** mapped on an 0.001au isodensity surface. The gradient (white to black) represents a potential of -793 kJ mol^{-1} to -551 kJ mol^{-1}.

7. $[UO_2Cl_3(NO_3)]^{2-}$ Computational Results

The crystallographic data of $(C_5H_5NBr)_2[UO_2Cl_3(NO_3)]$[16] was utilized and truncated so that the $[UO_2Cl_3(NO_3)]^{2-}$ anion could be treated to the same breadth of computational analyses that the plutonyl analogue was subjected. These analyses were performed at the same level of theory used to analyze **1**-**4** to demonstrate the consistency of our computational approach here and with our previous work.[17, 18] We note that the results of these analyses are consistent with established bonding trends in actinyl systems[19] and with the results of other related computational studies.[20]

Electrostatic Potential

The electrostatic potential of the $[UO_2Cl_3(NO_3)]^{2-}$ anion was calculated and mapped on an 0.001au isodensity surface (**Figure S21**, **S22** and **TableS11**) and the distribution thereof is comparable to that of the $[PuO_2Cl_3(NO_3)]^{2-}$ anion (**Table S7** and **Figure S15**). Variations in the magnitude of the potential magnitude from the uranyl to plutonyl anions are consistent with trends established in related $[AnO_2Cl_4]^{2-}$ (An = U, Np, Pu) systems.[17]

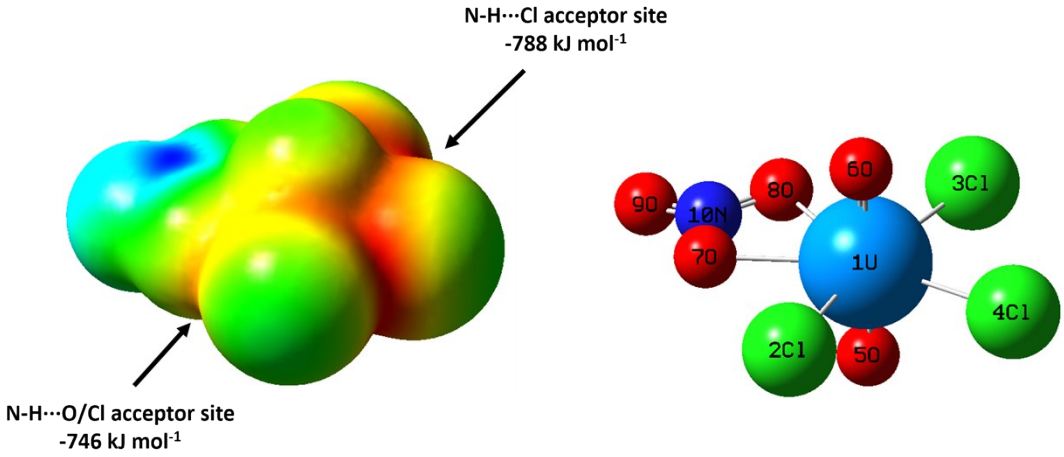

Figure S21. The electrostatic potential of the $[UO_2Cl_3(NO_3)]^{2-}$ anion is mapped on an 0.001au isodensity surface. The color scale represents a gradient from high potential magnitude (red, -785 kJ mol^{-1}) to a low potential magnitude (deep blue, -536 kJ mol^{-1}).

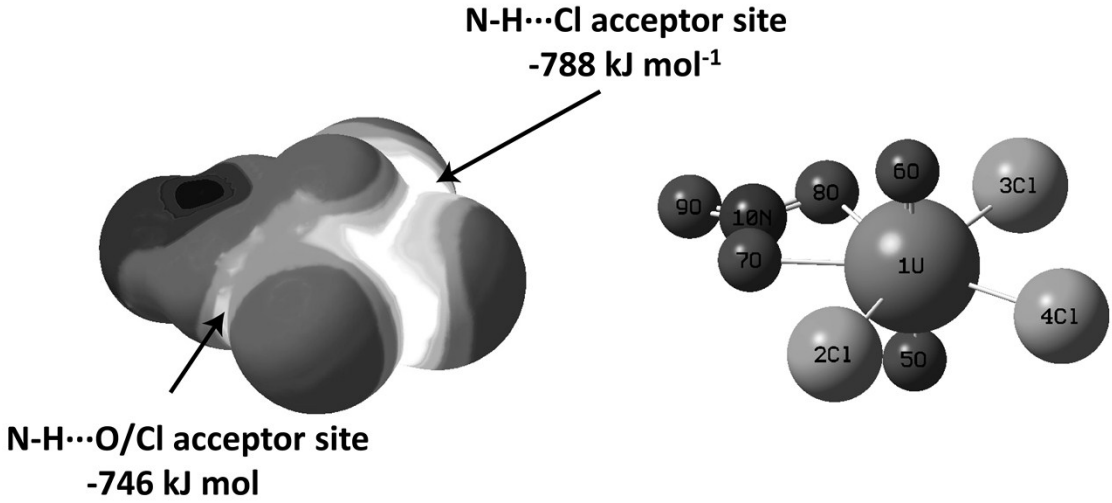

Figure S22. The electrostatic potential of the $[UO_2Cl_3(NO_3)]^{2-}$ anion is mapped on an 0.001au isodensity surface. The gradient (white-to-black) represents a magnitude from -785 kJ mol^{-1} to -536 kJ mol^{-1}.

Table S11. Electrostatic potential values at various points on the $[UO_2Cl_3(NO_3)]^{2-}$ anion. The atom labels correspond to those depicted in Figure S21.

Coaxial to the bond axis	Potential in kJ mol-1
U – Cl2	-649
U – Cl4	-659
U – Cl3	-654
Perpendicular to the bond axis	
U – Cl2	-725
U – Cl4	-732
U – Cl3	-721
Coaxial to the bond axis	
O6	-676
O5	-676
Perpendicular to the bond axis	
O6	-728
O5	-727
Regions between the Cl ligands	
Cl2 and Cl4	-785
Cl4 and Cl3 (accepts N-H···Cl hydrogen bond)	-788
NCI Acceptor Regions	
Between O7 and Cl2 (accepts N-H···Cl hydrogen bond)	-746

QTAIM Analysis

The QTAIM analysis revealed the U bonding picture in the $[UO_2Cl_3(NO_3)]^{2-}$ anion to be both covalent and ionic (**Table S12**). The electron density parameters indicate the axial $U{=}O_{yl}$ bonds are strong and covalent whereas the $U\text{-}O_{nitrate}$ and U-Cl bonds are polar and ionic. The U-Cl bonds have a minor covalent contribution as the electronic energy density (H) parameter is negative and the potential and local kinetic density ratio is ~1.2, which are both indicative of a partially covalent interaction. The $[UO_2Cl_3(NO_3)]^{2-}$ anion was truncated to the bare, uncoordinated uranyl cation and QTAIM analysis performed, the results of which again highlight the covalent nature of the $U{=}O_{yl}$ bond.

Table S12. Topological parameters of electron density of the $[UO_2Cl_3(NO_3)]^{2-}$ anion and the $[UO_2^{2+}]$ cation. All the electron density (ρ), its Laplacian ($\nabla^2\rho$), local kinetic energy density (G), potential energy density (V) and electronic energy density (H) parameters are in 10^3 au whereas the ellipticity (ε) and delocalization index (δ) are dimensionless.

Atoms	ρ	$\nabla^2\rho$	ε	$\delta(A,B)$	H_{BCP}	V_{BCP}	G_{BCP}	$\lvert V_{BCP}\rvert/G_{BCP}$
$[UO_2Cl_3(NO_3)]^{2-}$								
U1 - $O6_{yl}$	0.30306	0.33782	0.00719	1.85934	-0.2689	-0.6222	0.3533	1.7610
U1 - $O5_{yl}$	0.31370	0.33446	0.00635	1.87378	-0.2880	-0.6596	0.3716	1.7751
U1 - $O7_{(nitrate)}$	0.04700	0.17110	0.14034	0.22255	-0.0035	-0.0497	0.0463	1.0753
U1 - $O8_{(nitrate)}$	0.05091	0.18338	0.15245	0.23655	-0.0046	-0.0551	0.0505	1.0914
U1 - Cl2	0.06068	0.13527	0.04627	0.49314	-0.0120	-0.0578	0.0458	1.2615
U1 - Cl3	0.05947	0.13177	0.06416	0.48501	-0.0115	-0.0559	0.0444	1.2587
U1 - Cl4	0.05660	0.12827	0.05619	0.47642	-0.0103	-0.0527	0.0424	1.2431
$[UO_2]^{2+}$								
U1 – $O2_{yl}$	0.32409	0.33806	0.00022	2.24933	-0.30369	-0.69214	0.38844	1.7818
U1 – $O2_{yl}$	0.31330	0.34399	0.00002	2.24469	-0.28389	-0.65378	0.36988	1.7675

NLMO Results

The non-coordinated $[UO_2]^{2+}$ cation

The results of the NLMO analysis are consistent with a covalent bond picture. The hybrid atomic orbitals of the U atom are composed of d and f character whereas those of the O are nearly entirely p in character.

U=O_{yl} bond 1

18. (2.00000) 99.3944% BD (1) U 1- O 2
23.653% U 1 s(0.00%)p 1.00(0.35%)d99.99(36.32%)f99.99(63.25%)
76.194% O 2 s(0.00%)p 1.00(99.76%)d 0.00(0.23%)
0.154% O 3 s(0.20%)p99.99(97.11%)d12.25(2.47%)

19. (2.00000) 99.3960% BD (2) U 1- O 2
23.638% U 1 s(0.00%)p 1.00(0.35%)d99.99(36.28%)f99.99(63.29%)
76.209% O 2 s(0.00%)p 1.00(99.76%)d 0.00(0.23%)

20. (2.00000) 95.2533% BD (3) U 1- O 2
36.770% U 1 s(0.46%)p 0.29(0.14%)d47.44(21.96%)f99.99(77.40%)
61.524% O 2 s(12.92%)p 6.70(86.61%)d 0.04(0.45%)
1.706% O 3 s(13.15%)p 6.54(85.93%)d 0.07(0.92%)

U=O_{yl} bond 2

21. (2.00000) 99.3930% BD (1) U 1- O 3
23.629% U 1 s(0.00%)p 1.00(0.37%)d97.03(36.21%)f99.99(63.34%)
76.216% O 3 s(0.00%)p 1.00(99.77%)d 0.00(0.23%)

22. (2.00000) 99.3952% BD (2) U 1- O 3
23.611% U 1 s(0.00%)p 1.00(0.37%)d97.32(36.18%)f99.99(63.38%)
76.236% O 3 s(0.00%)p 1.00(99.77%)d 0.00(0.23%)

23. (2.00000) 95.2733% BD (3) U 1- O 3
36.532% U 1 s(0.41%)p 0.31(0.13%)d53.91(22.03%)f99.99(77.40%)
1.710% O 2 s(13.54%)p 6.32(85.52%)d 0.07(0.93%)
61.758% O 3 s(12.49%)p 6.97(87.07%)d 0.03(0.43%)

The $[UO_2Cl_3(NO_3)]^{2-}$ anion

The results of the NLMO analysis are consistent with a covalent U=O_{yl} and ionic U-Cl and U-$O_{nitrate}$ bond picture. The hybrid atomic orbitals of the U and O atoms in the U=O_{yl} bonds are composed of d and f character whereas those of the O are again nearly entirely p in character. The U-Cl bonds are dominated by Cl character (86 - 90% with HAO consisting of s and p character) as the HAO of the U metal center (which consisted of s, d and f character) has a minor contribution. A similar trend is observed in the analysis of the U-$O_{nitrate}$ bonding.

U = O_{yl} Bond 1

53. (2.00000) 98.3666% BD (1) U 1- O 5
21.200% U 1 s(0.06%)p 1.85(0.11%)d99.99(36.35%)f99.99(63.41%)
78.457% O 5 s(2.65%)p36.55(96.92%)

54. (2.00000) 98.7080% BD (2) U 1- O 5
20.459% U 1 s(0.00%)p 1.00(0.06%)d99.99(37.49%)f99.99(62.37%)
79.369% O 5 s(0.00%)p 1.00(99.59%)

55. (2.00000) 94.9237% BD (3) U 1- O 5
27.434% U 1 s(0.16%)p 1.20(0.19%)d99.99(17.23%)f99.99(82.37%)
71.264% O 5 s(23.72%)p 3.19(75.68%)
U = O_{yl} Bond 1

56. (2.00000) 98.3713% BD (1) U 1- O 6
21.116% U 1 s(0.07%)p 1.71(0.12%)d99.99(36.90%)f99.99(62.84%)

78.517% O 6 s(2.82%)p34.27(96.78%)

57. (2.00000) 98.7539% BD (2) U 1- O 6
20.304% U 1 s(0.00%)p 1.00(0.07%)d99.99(38.45%)f99.99(61.41%)
79.478% O 6 s(0.00%)p 1.00(99.61%)

58. (2.00000) 94.9563% BD (3) U 1- O 6
27.239% U 1 s(0.18%)p 1.13(0.20%)d98.60(17.56%)f99.99(82.02%)
1.158% O 5 s(29.05%)p 2.43(70.54%)
71.487% O 6 s(23.29%)p 3.27(76.15%)

U – Cl Bonds

49. (2.00000) 98.7415% BD (1) U 1-Cl 2
8.978% U 1 s(9.82%)p 0.02(0.20%)d 4.89(48.05%)f 4.27(41.92%)
90.753% Cl 2 s(13.13%)p 6.61(86.79%)

50. (2.00000) 96.8889% BD (2) U 1-Cl 2
10.319% U 1 s(14.93%)p 0.01(0.18%)d 3.45(51.56%)f 2.23(33.33%)
89.373% Cl 2 s(22.26%)p 3.49(77.63%)

51. (2.00000) 97.1472% BD (1) U 1-Cl 3
13.705% U 1 s(16.92%)p 0.01(0.13%)d 2.99(50.57%)f 1.91(32.37%)
85.894% Cl 3 s(36.40%)p 1.74(63.44%)

52. (2.00000) 97.1003% BD (1) U 1-Cl 4
13.480% U 1 s(19.19%)p 0.01(0.16%)d 2.69(51.61%)f 1.51(29.02%)
86.135% Cl 4 s(36.31%)p 1.75(63.54%)

U-$O_{nitrate}$ Bonds

59. (2.00000) 96.0481% BD (1) U 1- O 7
7.045% U 1 s(13.66%)p 0.01(0.20%)d 3.77(51.53%)f 2.53(34.59%)
90.520% O 7 s(31.66%)p 2.16(68.24%)
1.222% N 10 s(3.47%)p26.35(91.53%)d 1.35(4.71%)

60. (2.00000) 95.0958% BD (1) U 1- O 8
7.062% U 1 s(13.37%)p 0.01(0.19%)d 3.77(50.39%)f 2.69(36.02%)
90.449% O 8 s(32.33%)p 2.09(67.57%)
1.181% N 10 s(3.13%)p29.30(91.85%)d 1.50(4.72%)

Bond Valence Summation of the $[AnO_2Cl_3(NO_3)]^{2-}$ (An = U, Pu) anions

The Wiberg bond order of the An=O_{yl} bond was calculated and is consistent with the both the QTAIM and NLMO analyses and also established bond valence summations in related uranyl materials.[21]

The Uranyl Cation

Index matrix generated from Natural Atomic Orbital Methods:

Atom	1	2	3
1. U	0.0000	2.2169	2.2117
2. O	2.2169	0.0000	0.1929
3. O	2.2117	0.1929	0.0000

The $[UO_2Cl_3(NO_3)]^{2-}$ anion

Index matrix generated from Natural Atomic Orbital Methods:

Atom	1	2	3	4	5	6	7	8	9	10
1. U	0.0000	0.7835	0.7724	0.7616	2.0450	2.0348	0.3023	0.3136	0.0333	0.0162
2. Cl	0.7835	0.0000	0.0101	0.0093	0.0170	0.0171	0.0053	0.0058	0.0007	0.0038
3. Cl	0.7724	0.0101	0.0000	0.0092	0.0168	0.0168	0.0056	0.0063	0.0007	0.0045
4. Cl	0.7616	0.0093	0.0092	0.0000	0.0167	0.0168	0.0053	0.0055	0.0010	0.0004
5. O	2.0450	0.0170	0.0168	0.0167	0.0000	0.1744	0.0050	0.0052	0.0027	0.0040
6. O	2.0348	0.0171	0.0168	0.0168	0.1744	0.0000	0.0050	0.0051	0.0028	0.0040
7. O	0.3023	0.0053	0.0056	0.0053	0.0050	0.0050	0.0000	0.1846	0.2133	1.2910
8. O	0.3136	0.0058	0.0063	0.0055	0.0052	0.0051	0.1846	0.0000	0.2160	1.3052
9. O	0.0333	0.0007	0.0007	0.0010	0.0027	0.0028	0.2133	0.2160	0.0000	1.4396
10. N	0.0162	0.0038	0.0045	0.0004	0.0040	0.0040	1.2910	1.3052	1.4396	0.0000

The $[PuO_2Cl_3(NO_3)]^{2-}$ anion

Index matrix generated from Natural Atomic Orbital Methods:

Atom	1	2	3	4	5	6	7	8	9	10
1. Pu	0.0000	0.0130	2.0628	2.0511	0.6933	0.2808	0.2640	0.0309	0.7102	0.7197
2. Cl	0.0130	0.0000	0.0029	0.0030	0.0006	1.3003	1.3037	1.4380	0.0044	0.0033
3. Cl	2.0628	0.0029	0.0000	0.3290	0.0179	0.0058	0.0054	0.0022	0.0184	0.0188
4. Cl	2.0511	0.0030	0.3290	0.0000	0.0179	0.0056	0.0053	0.0024	0.0186	0.0188
5. O	0.6933	0.0006	0.0179	0.0179	0.0000	0.0057	0.0056	0.0009	0.0084	0.0085
6. O	0.2808	1.3003	0.0058	0.0056	0.0057	0.0000	0.1876	0.2164	0.0064	0.0064
7. O	0.2640	1.3037	0.0054	0.0053	0.0056	0.1876	0.0000	0.2183	0.0062	0.0049
8. O	0.0309	1.4380	0.0022	0.0024	0.0009	0.2164	0.2183	0.0000	0.0008	0.0007
9. O	0.7102	0.0044	0.0184	0.0186	0.0084	0.0064	0.0062	0.0008	0.0000	0.0109
10. N	0.7197	0.0033	0.0188	0.0188	0.0085	0.0064	0.0049	0.0007	0.0109	0.0000

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