

Supporting Information for:

Non-aqueous Neptunium and Plutonium Redox Behaviour in THF – Access to a Rare Np(III) Synthetic Precursor

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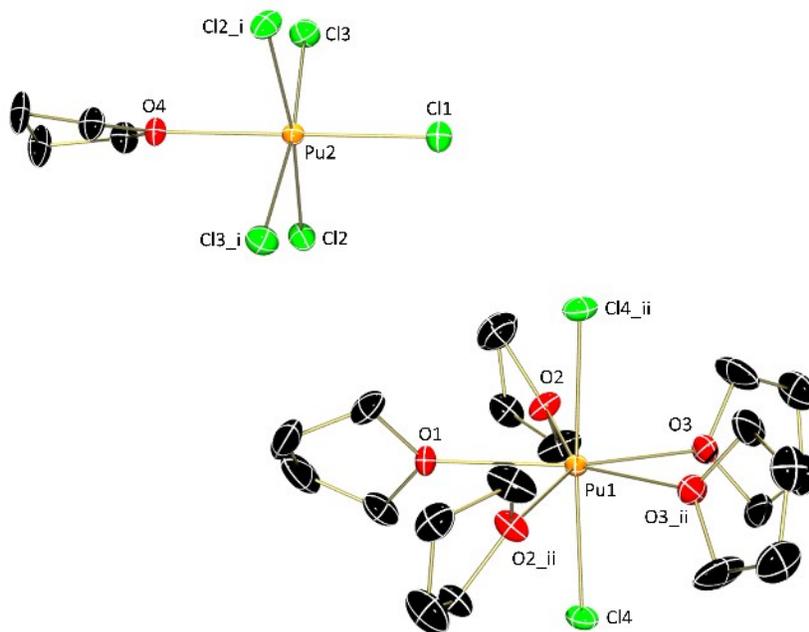


Figure S1. Molecular structure of $[\text{PuCl}_2(\text{THF})_5][\text{PuCl}_5(\text{THF})]$ shown with 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

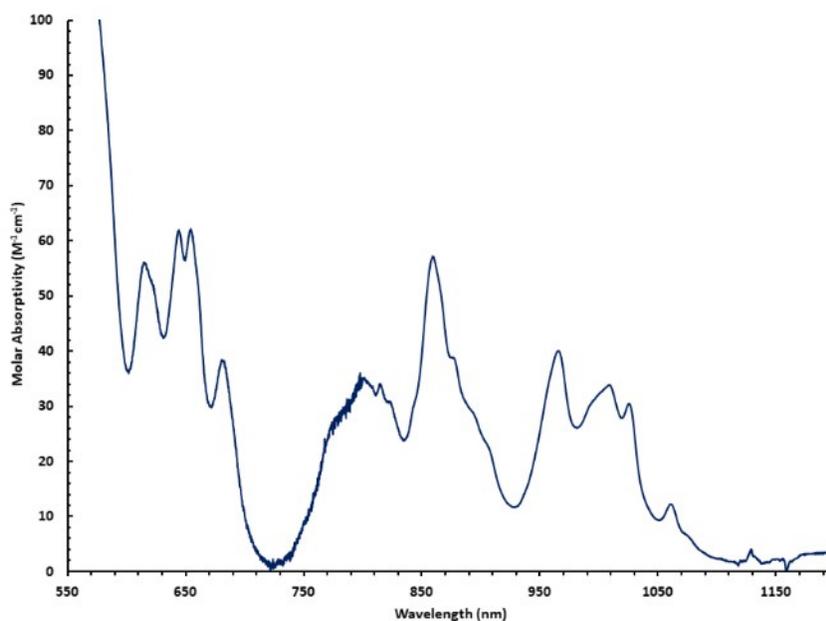


Figure S2. Vis-NIR spectrum of $\text{NpCl}_3(\text{py})_4$ in pyridine at ambient temperature. Molar absorptivities were calculated based on dissolution of 2.1 mg $\text{NpCl}_3(\text{py})_4$ into 1.694 g of pyridine.

General Experimental Information

Caution! ^{237}Np ($t_{1/2} = 2.14 \times 10^6$ y) and ^{239}Pu ($t_{1/2} = 2.41 \times 10^4$ y) are high specific-activity α -particle emitting radionuclides and pose serious health risks if not properly contained (as well as $\alpha/\beta/\gamma$ -radiation hazards from their daughter products). This research was conducted at specialized radiological facilities at Los Alamos National Laboratory, which were designed with appropriate analyses of hazards and implementation of controls for the safe handling of these materials. Multiple levels of containment were utilized when appropriate for safety reasons, and all free-flowing solids containing neptunium or plutonium were handled in negative-pressure gloveboxes. Stock solutions of ^{237}Np and Pu of predominant ^{239}Pu isotopic composition were obtained from internal sources at Los Alamos National Laboratory. Due to these radiological hazards, elemental analyses of complexes containing Np or Pu radioisotopes were not possible.

For this study, all reactions were performed under an anaerobic, anhydrous atmosphere inside an Mbraun Labmaster 130 helium atmosphere drybox. The inert atmosphere was maintained with a standalone Vacuum Atmosphere Genesis oxygen and moisture removal system. All solvents were purchased as anhydrous grade, and were further dried over a mixture of 3 Å and 4 Å molecular sieves for several days before use. THF was additionally dried by storing over NaK for several days before it was filtered through dry alumina onto a mixture of 3 Å and 4 Å molecular sieves. $\text{NpCl}_4(\text{DME})_2$,¹ $\text{PuCl}_4(\text{DME})_2$,¹ and CsC_8 ² were prepared according to literature procedures.

The solution phase electronic absorption spectrum of $\text{NpCl}_3(\text{py})_4$ was collected in a screw-capped quartz cuvette (1 cm path length) that was loaded in a transuranic glovebox using Parafilm to protect the exterior surface of the cuvette and cap from radioactive contamination (parafilm removed in fumehood prior to data acquisition). The solution was prepared by dissolving 2.1 mg of dried crystalline material in 1.694 g of pyridine ($\sim 1.8 \times 10^{-3}$ M). The spectrum was collected at ambient temperature using a Varian Cary 6000i UV/vis/NIR spectrometer.

Isolation of $[\text{PuCl}_2(\text{THF})_5][\text{PuCl}_5(\text{THF})]$. $\text{PuCl}_4(\text{DME})_2$ (~ 3 mg) was dissolved in THF (~ 1 mL) and was stirred for one hour. No obvious change to the golden colour was noted. This solution was layered with pentane (~ 0.5 mL) and cooled to -35 °C, producing X-ray quality

crystals overnight. Analysis of one of these crystals revealed a molecular formula of $[\text{PuCl}_2(\text{THF})_5][\text{PuCl}_5(\text{THF})]$ instead of the expected THF adduct of plutonium tetrachloride.

Isolation of $\text{NpCl}_4(\text{THF})_3$. $\text{NpCl}_4(\text{DME})_2$ (20.0 mg, 0.0358 mmol) was dissolved in THF (~2 mL) and was stirred overnight. No obvious change to the solution colour was noted after approximately 16 hours. This solution was layered with pentane (~1 mL) and cooled to $-35\text{ }^\circ\text{C}$, producing X-ray quality crystals within 24 hours. Analysis of one of these salmon coloured crystals confirmed the molecular composition as $\text{NpCl}_4(\text{THF})_3$.

Preparation of $\text{NpCl}_3(\text{THF})_n$. $\text{NpCl}_4(\text{DME})_2$ (20.0 mg, 0.0358 mmol) was dissolved in THF (~2 mL) and stirred for 5 minutes. CsC_8 (8.2 mg, 0.036 mmol) was slowly added as a solid, resulting in a colour change of the salmon solution to green. This solution was stirred for one hour before it was filtered, resulting in a translucent yellow solution, which was then concentrated *in vacuo* to afford a yellow residue. This residue was redissolved in a minimal amount of THF (<1 mL), and the product was precipitated with addition of ~10 mL of pentane. After cooling to $-35\text{ }^\circ\text{C}$, the supernatant was decanted, and the crystalline product was dried *in vacuo* to a free-flowing yellow crystalline powder. 9.9 mg were collected, which would correspond to a 49% yield if the product were $\text{NpCl}_3(\text{THF})_3$ or a 44% yield if the product were $\text{NpCl}_3(\text{THF})_4$ (although crystalline the material did not yield single-crystals of sufficient size for X-ray structural). Given the desire to isolate pure products as a basis for future reactivity studies we focused on lower (but still synthetically useful) crystalline yields rather than higher yielding crude product determinations. Furthermore, since the exact molecular formula was uncertain, an electronic absorption spectrum was not recorded, and all of the material generated was utilized in pursuit of a derivative that produced single-crystals suitable for X-ray diffraction, as detailed below.

Isolation of $\text{NpCl}_3(\text{py})_4$. The crystalline $\text{NpCl}_3(\text{THF})_n$ material from the synthesis of $\text{NpCl}_3(\text{THF})_n$ (9.9 mg) was dissolved in pyridine (~2 mL), layered with Et_2O , and cooled to $-35\text{ }^\circ\text{C}$, resulting in X-ray quality single crystals suitable for structural determination of $\text{NpCl}_3(\text{py})_4 \cdot 2\text{Et}_2\text{O}$.

General Crystallographic Details

To ensure safe handling of radioisotopes during X-ray crystallographic experiments, crystals of each compound were prepared with appropriate layers of containment. Single crystals of $[\text{PuCl}_2(\text{THF})_5][\text{PuCl}_5(\text{THF})]$, $\text{NpCl}_4(\text{THF})_3$, and $\text{NpCl}_3(\text{py})_4 \cdot 2\text{Et}_2\text{O}$ suitable for X-ray diffraction, were coated with Paratone-N oil in a glovebox and mounted inside 0.5 mm capillary tubes, which were subsequently sealed with hot capillary wax. The samples were removed from the glovebox, and the exterior surfaces were coated in a thin film of acrylic dissolved in ethyl acetate (Hard as Nails[®]) to provide structural integrity and appropriate containment of the materials. These contained samples were mounted on the goniometer head on a Bruker D8 diffractometer.

Initial examination and data collection were performed with $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). All data were collected at 100 K. Data were collected and reflections were indexed and processed using the APEX II software.³ The data were corrected for absorption using the SADABS program.⁴ Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using the SAINT+ software.⁵ Structure solution and refinement were performed using SHELXTL software. All hydrogen atom positions were idealized and rode on the atom to which they were attached. Final refinements include anisotropic temperature factors on all non-hydrogen atoms. Additional data collection and refinement parameters are given in Tables S1-S3.

Local name: apx2586

CCDC: 1830523

Table S1. Crystallographic Details for $[\text{PuCl}_2(\text{THF})_5][\text{PuCl}_5(\text{THF})]$.

Crystal data	
Chemical formula	$\text{Pu}_2\text{Cl}_7\text{C}_{24}\text{H}_{48}\text{O}_6$
M_r	1158.81
Crystal system, space group	Monoclinic, $P2/c$
Temperature (K)	100
a, b, c (Å)	12.264(3), 11.172(3), 13.938(4)
V (Å ³)	1850.0(8)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	4.07
Crystal size (mm)	0.34 x 0.34 x 0.27
Data collection	
Diffractometer	Bruker D8 with ApexII CCD
Absorption correction	Multi-scan <i>SADABS</i> v. 2.03 (Sheldrick, 2008)
T_{\min}, T_{\max}	0.192, 0.253
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	20230, 4435, 4006
R_{int}	0.040
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.674
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.032, 0.066, 1.74
No. of reflections	4435
No. of parameters	179
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	1.57, -1.26

Computer programs: *APEX II*, v. 7.0 (Bruker AXS, 2009), *SAINT+*, v. 7.66a (Bruker AXS, 2009), *SHELXS* 2013/1 (Sheldrick, 2013), *SHELXL* 2014/7 (Sheldrick, 2014), *SHELXTL*, v. 2014/7, (Bruker AXS, 2014).

Local name: apx2580a

CCDC: 1830524

Table S2. Crystallographic Details for $\text{NpCl}_4(\text{THF})_3$.

Crystal data	
Chemical formula	$\text{NpCl}_4\text{C}_{12}\text{H}_{24}\text{O}_3$
M_r	545.06
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	100
a, b, c (Å)	7.8064(13), 14.381(3), 8.4636(15)
β (°)	100.8372(19)
V (Å ³)	933.2(3)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	6.14
Crystal size (mm)	0.40 x 0.30 x 0.08
Data collection	
Diffractometer	Bruker D8 with APEXII CCD
Absorption correction	Multi-scan <i>SADABS</i> v. 2.03 (Sheldrick, 2008)
T_{\min}, T_{\max}	0.086, 0.612
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10636, 4354, 3963
R_{int}	0.039
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.672
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.027, 0.055, 0.98
No. of reflections	4354
No. of parameters	200
No. of restraints	15
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	1.22, -0.89
Absolute structure	Refined as an inversion twin
Absolute structure parameter	0.38(2)

Computer programs: *APEX II*, v. 7.0 (Bruker AXS, 2009), *SAINT+*, v. 7.66a (Bruker AXS, 2009), *SHELXS* 2013/1 (Sheldrick, 2013), *SHELXL* 2014/7 (Sheldrick, 2014), *SHELXTL*, v. 2014/7, (Bruker AXS, 2014).

Local name: apx2588a_sq

CCDC: 1830525

Table S3. Crystallographic Details for $\text{NpCl}_3(\text{py})_4 \cdot 2\text{Et}_2\text{O}$.

Crystal data	
Chemical formula	$\text{NpCl}_3\text{C}_{28}\text{H}_{40}\text{N}_4\text{O}_2$
M_r	807.99
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	100
a, b, c (Å)	12.5752(8), 15.7756(10), 15.1347(14)
β (°)	108.7108(7)
V (Å ³)	2843.8(4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	3.97
Crystal size (mm)	0.40 x 0.12 x 0.12
Data collection	
Diffractometer	Bruker D8 with APEXII CCD
Absorption correction	Multi-scan <i>SADABS</i> v. 2.03 (Sheldrick, 2008)
T_{\min}, T_{\max}	0.304, 0.621
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16224, 3452, 3024
R_{int}	0.031
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.673
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.022, 0.046, 1.07
No. of reflections	3452
No. of parameters	128
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	1.38, -0.51

Computer programs: *APEX II*, v. 7.0 (Bruker AXS, 2009), *SAINT+*, v. 7.66a (Bruker AXS, 2009), *SHELXS* 2013/1 (Sheldrick, 2013), *SHELXL* 2014/7 (Sheldrick, 2014), *SHELXTL*, v. 2014/7, (Bruker AXS, 2014).

References

1. S. D. Reilly, J. L. Brown, B. L. Scott and A. J. Gaunt *Dalton Trans.*, 2014, **43**, 1498.
2. D. Savoia, C. Trombini and A. Umani-Ronchi *Pure & Appl. Chem.*, 1985, **57**, 1887.
3. APEX II, version 7.0, **2009**, Bruker AXS, Inc., Madison, Wisconsin 53719.
4. SADABS program, version 2.03, **2008**, George Sheldrick, University of Göttingen, Germany.
5. SAINT+ software, version 7.66a, **2009**, Bruker AXS, Inc., Madison, Wisconsin 53719.