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

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Redox behavior and preferences in common solvents utilized for nonaqueous Np and Pu synthetic chemistry are poorly understood. Solvent exchange of $NpCl_4(DME)_2$ with THF proceeds simply to yield $NpCl_4(THF)_3$, whereas $PuCl_4(DME)_2$ is unstable in THF, partially decomposing to the mixed valent $[Pu^{III}Cl_2(THF)_5][Pu^{IV}Cl_5(THF)]$ salt. Reduction of $NpCl_4(THF)_3$ with CsC_8, using pyrdine to 'trap' the product, affords $NpCl_3(py)_4$, the only example of a structurally characterized solvated trivalent neptunium halide, while avoiding scarce Np^0 as the entry route.

In the realm of actinide chemistry, studies on uranium and thorium (primarily utilizing the low-specific activity ^{238}U and ^{232}Th α-particle emitting radioisotopes) have dominated.[1] Far less progress has been realized for nuclear fuel cycle relevant transuranic (TRU) elements (Np-Cm) in terms of fundamental research, largely on account of the reduced availability of these elements and the specialized radiological facilities needed to safely handle the TRU materials that are available, which usually comprise high specific-activity α-particle emitters such as ^{237}Np and ^{239}Pu.[1,2]

Recently, neptunium and plutonium have experienced significant advances in the area of nonaqueous chemistry, as demonstrated by the number of new reviews on the topic.[2–4] This has been motivated in part by the development of new nonaqueous actinide-solvento halide starting materials prepared from both An-oxide and An^0 (An = actinide) sources.[5–9] These materials have facilitated the discovery of new oxidation states[9,10] and new bonding motifs including a neptunium bis(imido) complex[11] and neptunium (III) cyclopentadienyl complexes.[9] A parallel can be drawn from the synthesis of $UI_3(THF)_4$ from U^0 by Zwick, Sattelberger, and Clark in 1994, which greatly facilitated the study of low valent uranium chemistry for years to come.[5]

Despite the moderate recent progress, nonaqueous studies of neptunium and plutonium chemistry are still constrained by the limited number of entry routes into well-defined, organic-soluble, starting materials in a specific desired oxidation state. Access to Pu(III) chemistry is typically achieved by oxidation of Pu metal or utilizing $PuCl_3$, sources that are relatively common for facilities that research Pu chemistry. However, neutral, nonaqueous Pu(IV) molecules as synthetic precursors are barely developed, with $PuCl_4(DME)_2$ the only example in the literature.[8] Previous observations have pointing towards difficulty in accessing Pu(IV) under inert atmospheric conditions in dry solvents – for example, oxidation of Pu metal with iodine or bromine in THF does not proceed past the +3 oxidation state,[7] while partial reduction of Pu(VI) or Pu(IV) in THF has been observed without addition of a reductant. In the case of Np, the metal form is very scarce, restricting the utility of the oxidative entry route into Np(III) chemistry. However, solid NpO_2 and acidic aqueous stock solutions of Np(IV) are more readily available, and via dehydration routes, can be converted into materials such as $NpCl_4$ and $NpCl_4(DME)_2$ as suitable reagents for inert atmosphere synthetic chemistry.[8,9] A few studies that reduce Np(IV) to generate Np(III) in situ have proven fruitful, but the nature of the Np(III) intermediates are not well-defined. In order to more widely study Np(III) chemistry, development of a facile reductive route that unambiguously yields a Np(III) precursor of known molecular structure would significantly aid progress in the field.

Herein, we report the solvent exchange and reduction behavior of the An(IV) transuranic starting materials, $PuCl_4(DME)_2$ and $NpCl_4(DME)_2$, in tetrahydrofuran (THF) and note the stark differences between these two isostructural compounds.

Our studies commenced with experiments to understand the basic solvent exchange chemistry of $PuCl_4(DME)_2$ and $NpCl_4(DME)_2$ with THF. Though these transformations seem trivial, coordinated solvent can be an important synthetic nuance in directing product identity. In fact, unwanted side

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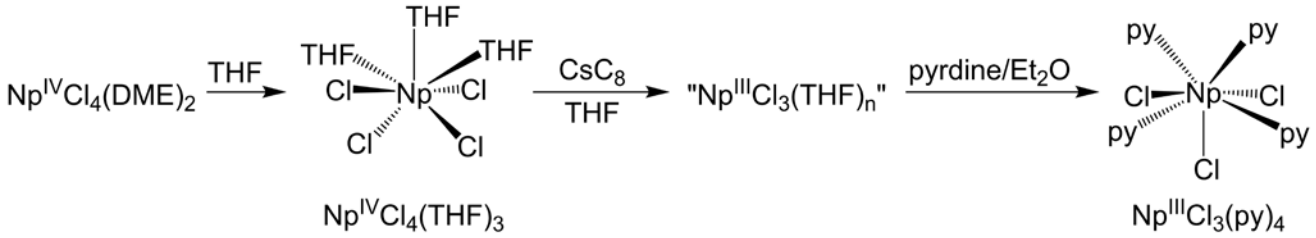
Electronic Supplementary Information (ESI) available: Additional experimental details and CIF and structural data. See DOI: 10.1039/x0xx00000x



Scheme 1. Synthetic route and crystallization conditions that lead to $NpCl_4(THF)_3$ and $NpCl_3(py)_4$.

reactivity of DME was recently reported with neptunium complexes under reducing conditions.[12] Additionally, the chelating nature of DME may be undesirable to other studies that rely on solvent lability to open coordination sites for substrate. Well characterized solution routes to highly soluble solvent adducts of $NpCl_4$ or $PuCl_4$ other than with DME have not yet been reported.

In a negative pressure helium drybox, $PuCl_4(DME)_2$ was dissolved in THF, maintaining the original golden color. Layering the solution with pentane and cooling to -35 °C overnight produced dichroic crystals suitable for X-ray crystallography. Refinement of the data revealed a monoclinic P2/*c* space group. Instead of the expected THF adduct, the structure was the mixed valent plutonium salt $[Pu^{III}Cl_2(THF)_5][Pu^{IV}Cl_5(THF)]$, containing independent Pu(III) and Pu(IV) centers (Figure S1). This product, obtained from partial, spontaneous reduction of Pu(IV) (likely through disproportionation) in THF solutions, has been reported as a decomposition product twice before, once from Pu(IV) carbonate in THF/HCl and once from hexane washes of high valent $[PuO_2Cl_2(THF)_2]_2$ synthesized in THF (see SI for X-ray data).[7] Isolation of the mixed valent product for the third time highlights that Pu(IV) is prone to reduction in THF. This unusual redox chemistry is counter to examples with other tetravalent

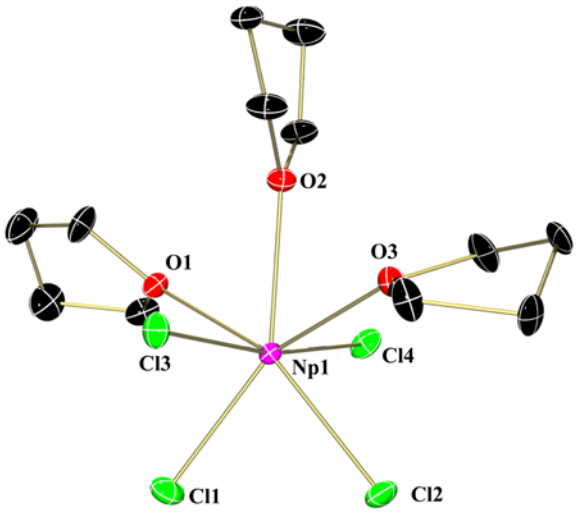


Figure 1. Molecular structure of $NpCl_4(THF)_3$ shown at 30% probability ellipsoids. Hydrogen atoms and disorder have been omitted for clarity.

actinides earlier in the f-block series, namely U(IV) and Th(IV), which exhibit remarkable thermal stability in most organic solvents. As the actinide series is traversed, increased stability of An(III) ions is expected, but Pu appears to be a transitional element, with Pu(IV) dominant in aqueous/aerobic environments but much more difficult to access in organic solvent/anaerobic enviroments. Instability of Pu(IV) in THF demonstrates the important of $PuCl_4(DME)_2$ as a well-defined starting material to closely parallel U(IV) entry routes that utilize neutral halide-solvento starting materials.[1,13]

Contrastingly, dissolution of $NpCl_4(DME)_2$ in THF resulted in no obvious change to the initial salmon-pink color. Layering this solution with pentane and cooling it to -35 °C overnight produced salmon colored crystals suitable for X-ray crystallography. Refinement of the data revealed that the compound crystallized in a monoclinic $P2_1$ space group, isomorphous to the structural parameters of $UCl_4(THF)_3$ reported by Sauer and Van Der Sluys.[14] The solid-state structure comprises a Np(IV) metal centre in a pseudo pentagonal bipyramidal geometry with axial chlorides, similar to that of $UCl_4(THF)_3$ (Scheme 1, Figure 1, Table 1). The Np-Cl distances range from 2.568(2) to 2.607(2) Å, similar to those in $NpCl_4(DME)_2$ (2.5878(9)-2.6224(9) Å),[8] and in $UCl_4(THF)_3$ (2.578(3)-2.612(3) Å).[14]

With the successful isolation of $NpCl_4(THF)_3$, a new Np(IV) neutral, organic-soluble, starting material, we rationalized that this complex, would be ideal for *in situ* reduction routes to trivalent neptunium chemistry without the complication of possible DME reduction to methoxide.[12] Reduction of binary $NpCl_4$ has been demonstrated by Walter, Arnold, and coworkers, who treated polymeric $NpCl_4$ suspension in Et_2O with sodium amalgam to create a highly reactive form of '$NpCl_3$'.[9] Although this material is poorly soluble and undoubtedly polymeric like other forms of anhydrous AnX_3,[15,16] it has proven useful in metathesis reactions as demonstrated by synthesis of homoleptic Np(III) cyclopentadienide complexes. The aim our reduction study was to gain a better understanding of reduction processes by generating an isolable Np(III) starting material of known molecular formula and structure, thus offering a reliable route into nonaqueous, trivalent neptunium chemistry.

As a reductant we chose CsC_8 since the stoichiometry could be more easily controlled on a small scale than KC_8 (a more common reductant), and the CsCl and graphite byproducts could be easily separated from the product. Slow addition of

one equivalent of CsC_8 to a stirring solution of $NpCl_4(THF)_3$ in THF caused a color change from salmon to green. After filtering to remove graphite and CsCl, the solution appeared bright yellow and was subsequently concentrated *in vacuo* to a bright yellow, free-flowing powder. This powder, presumably the THF adduct of $NpCl_3$, was highly soluble in THF but insoluble in pentane. Single-crystals suitable for X-ray diffraction were not obtained, precluding structural confirmation of the putative '$NpCl_3(THF)_x$' product. Starting with 20.0 mg of $NpCl_4(DME)_2$ yielded 9.9 mg of this recrystallized microcrystalline material – corresponding to crystalline yields of 44% if $NpCl_3(THF)_4$ or 49% if $NpCl_3(THF)_3$– in either case the yield is synthetically useful and not a minor product. It is worth noting that early-lanthanide trichlorides, with large ionic radii, take the formula $LnCl_3(THF)_4$, while smaller, later lanthanide trichlorides have the formula $LnCl_3(THF)_3$.[17–19]

There are currently no reports of structurally characterized THF adducts of any An(III) chlorides, including uranium. In fact, the recent accounts of dimeric $[UCl_3(py)_4]_2$ and trimeric $[UCl(py)_4(\mu\text{-}Cl)_3U(py)_2(\mu\text{-}Cl)_3UCl_2(py)_3]$ (py = pyridine) by Meyer and coworkers represented the first crystallographically characterized nonaqueous complexes of UCl_3 in 2014.[20] We therefore attempted to trap the "$NpCl_3$" product with pyridine in an analogous fashion. Dissolution of the yellow powder in dry pyridine caused an immediate color change to orange. This solution was layered with Et_2O and cooled to -35 °C, producing orange crystals overnight that were suitable for X-ray crystallography. Refinement of the data revealed that the compound crystallized in a monoclinic C2/*c* space group, and

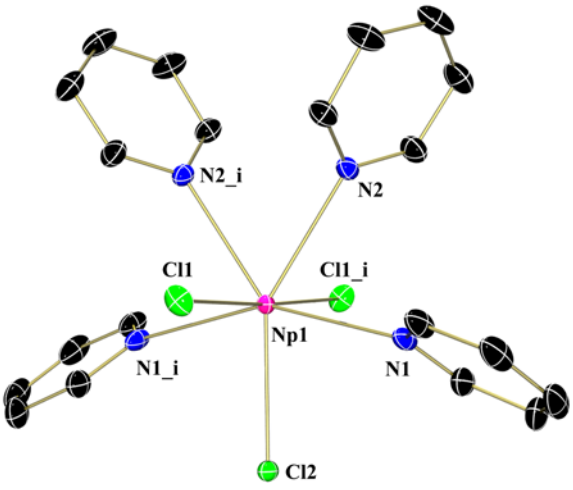


Figure 2. Molecular structure of $NpCl_3(py)_4$ shown at 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

the structure was composed of monomeric $NpCl_3(py)_4$ in a pseudo trigonal bipyramidal geometry with axial chloride ligands (Figure 2).

Notably, the structure of $NpCl_3(py)_4$ is monomeric, while the uranium analogue, grown from similar crystallization conditions, is dimeric through two chloride atoms.[20] The Np-Cl distances range from 2.7097(7) to 2.7303(9) Å, slightly longer than the Np(III)-Cl distance of 2.6694(9) Å in $[(L^{Ar})NpCl]$ (L^{Ar} = *trans*-calix[2]benzene[2]pyrrole).[12] Not surprisingly, the Np-Cl distances in $NpCl_3(py)_4$ are approximately 0.1-0.15 Å longer than the distances in $NpCl_4(THF)_3$ (Table 1), similar to difference in ionic radii of Np(III) vs. Np(IV).[19] The Np-pyridine distances represent the only known Np(III) dative nitrogen distances and range from 2.620(2) to 2.641(2) Å.

Table 1. Np-Cl and Np-solvent (solvent = coordinated THF or py) distances (in Å) for $NpCl_4(THF)_3$ and $NpCl_3(py)_4$.

Bond	$NpCl_4(THF)_3$	$NpCl_3(py)_4$
Np-Cl_{ax}	2.568(2)	2.7097(7)
Np-Cl_{ax}	2.575(2)	2.7097(7)
Np-Cl_{eq}	2.595(2)	2.7303(9)
Np-Cl_{eq}	2.607(2)	--
Np-solvent	2.452(6)	2.620(2)
Np-solvent	2.461(5)	2.620(2)
Np-solvent	2.495(6)	2.641(2)
Np-solvent	--	2.641(2)

$NpCl_3(py)_4$ was also examined by electronic absorption spectroscopy in the visible and near-IR regions. $NpCl_3(py)_4$ was dissolved in dry pyridine to make a $1.8x10^{-3}$ M solution, and the spectrum was taken with the solution sealed in a quartz screw-capped cuvette. The spectrum, shown in Figure 3, shows the electronic "fingerprint" for trivalent neptunium ions with weakly intense 5f-5f transitions in the region of 600-1100 nm. There are striking similarities with both the spectrum of Np(III) ions in perchloric acid[21] and also the spectrum of $NpI_3(THF)_4$ in THF.[5] This further validates the oxidation state of Np(III) in $NpCl_3(py)_4$.

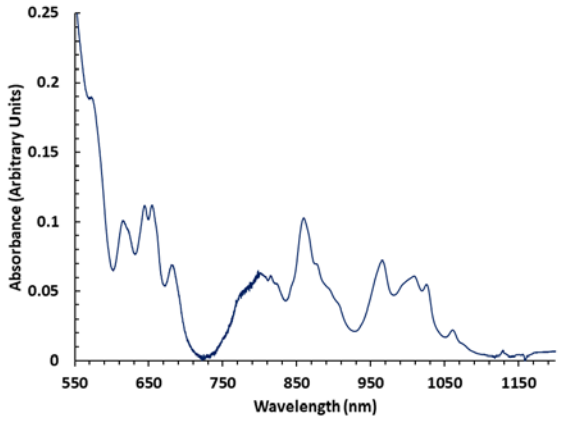


Figure 3. Vis-NIR spectrum of $NpCl_3(py)_4$ in pyridine ($1.8x10^{-3}$ M) at ambient temperature.

In summary, we report solvent exchange and redox properties of the transuranic starting materials, $NpCl_4(DME)_2$ and $PuCl_4(DME)_2$, in THF. DME is readily displaced in $NpCl_4(DME)_2$ forming the THF adduct $NpCl_4(THF)_3$, which was crystallographically characterized. Contrastingly, $PuCl_4(DME)_2$ was found to be unstable with respect to partial reduction in THF, leading to structural identification of the mixed valent plutonium salt, $[PuCl_2(THF)_5][PuCl_5(THF)]$. This salt has now

been reported three times, which highlights the driving force for the formation of Pu(III) under nonaqueous/inert atmosphere conditions. Reduction of $NpCl_4(THF)_3$ with CsC_8 allowed for the isolation of a yellow powder that was presumed to be a molecular THF adduct of $NpCl_3$, and expected to be of great utility for subsequent reactivity studies. Confirmation of reduction to an '$NpCl_3$' species was achieved by 'trapping' the product with pyridine, generating monomeric $NpCl_3(py)_4$, a formulation confirmed by single-crystal X-ray diffraction. Notably, the structure contains the only known Np(III) neutral nitrogen distances. Electronic absorption spectroscopy supports the assignment of the oxidation state as Np(III). These highly soluble, molecular $NpCl_3$-solvento molecules provide easy access to molecular Np(III) chemistry that has previously been hindered by the scarce availability of neptunium metal, and in situ generation routes for which the identity of the reduction products to be used as synthons are not known.

Experimental studies were supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division, Heavy Element Chemistry Program (Contract DE-AC52-06NA25396 to A.J.G. and Contract DE-SC0008479 to S.C.B.) and the G.T. Seaborg Institute at Los Alamos National Laboratory (LANL) for a summer student Fellowship (to S.A.P.). We are grateful to Dr. Aaron Tondreau and Dr. James Boncella for technical support.

Conflicts of interest

There are no conflicts to declare.

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Supporting Information for:

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

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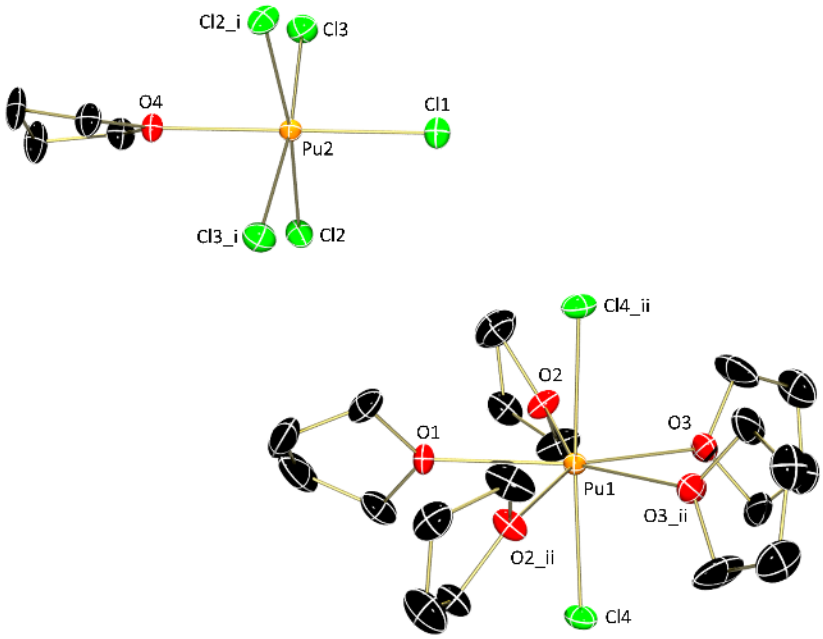

Figure S1. Molecular structure of $[PuCl_2(THF)_5][PuCl_5(THF)]$ shown at 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

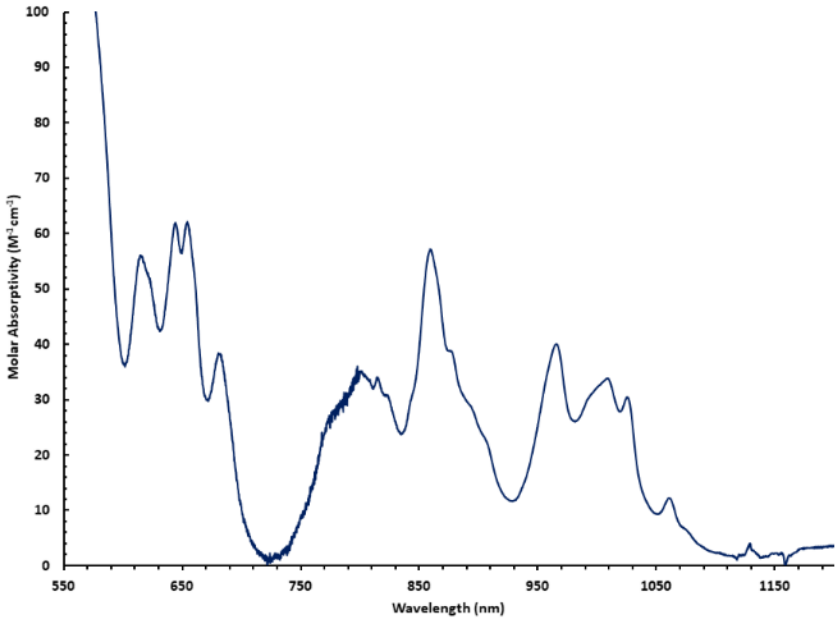

Figure S2. Vis-NIR spectrum of $NpCl_3(py)_4$ in pyridine at ambient temperature. Molar absorptivities were calculated based on dissolution of 2.1 mg $NpCl_3(py)_4$ into 1.694 g of pyridine.

General Experimental Information

Caution! ^{237}Np ($t_{1/2}$ = 2.14 x 10^6 y) and ^{239}Pu ($t_{1/2}$ = 2.41 x 10^4 y) are high specific-activity α-particle emitting radionuclides and pose serious health risks if not properly contained (as well as α/β/γ-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. $NpCl_4(DME)_2$,[1] $PuCl_4(DME)_2$,[1] and CsC_8[2] were prepared according to literature procedures.

The solution phase electronic absorption spectrum of $NpCl_3(py)_4$ 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 (~1.8 x 10^{-3} M). The spectrum was collected at ambient temperature using a Varian Cary 6000i UV/vis/NIR spectrometer.

Isolation of $[PuCl_2(THF)_5][PuCl_5(THF)]$. $PuCl_4(DME)_2$ (~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 $[PuCl_2(THF)_5][PuCl_5(THF)]$ instead of the expected THF adduct of plutonium tetrachloride.

Isolation of $NpCl_4(THF)_3$. $NpCl_4(DME)_2$ (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 °C, producing X-ray quality crystals within 24 hours. Analysis of one of these salmon coloured crystals confirmed the molecular composition as $NpCl_4(THF)_3$.

Preparation of $NpCl_3(THF)_n$. $NpCl_4(DME)_2$ (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 °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 $NpCl_3(THF)_3$ or a 44% yield if the product were $NpCl_3(THF)_4$ (although crystalline the material did not yield single-crystals of sufficient size for X-ray structural determination). 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.

Isolation of $NpCl_3(py)_4$. The crystalline $NpCl_3(THF)_n$ material from the synthesis of $NpCl_3(THF)_n$ (9.9 mg) was dissolved in pyridine (~2 mL), layered with Et_2O, and cooled to -35 °C, resulting in X-ray quality single crystals suitable for structural determination.

General Crystallographic Details

To ensure safe handling of radioisotopes during X-ray crystallographic experiments, crystals of each compound were prepared with appropriate layers of contamination. Single crystals of $[PuCl_2(THF)_5][PuCl_5(THF)]$, $NpCl_4(THF)_3$, and $NpCl_3(py)_4$ 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 Mo Kα radiation (λ = 0.71073 Å). 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 $[PuCl_2(THF)_5][PuCl_5(THF)]$.

Crystal data	
Chemical formula	$Pu_2Cl_7C_{24}H_{48}O_6$
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 Kα
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 *SADABS* 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
$(\sin \theta/\lambda)_{max}$ (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
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (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 $NpCl_4(THF)_3$.

Crystal data	
Chemical formula	$NpCl_4C_{12}H_{24}O_3$
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 Kα
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 *SADABS* 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
$(\sin \theta/\lambda)_{max}$ (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
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (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 $NpCl_3(py)_4$

Crystal data	
Chemical formula	$NpCl_3C_{20}H_{20}N_4$
M_r	659.76
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 Kα
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 *SADABS* 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
$(\sin \theta/\lambda)_{max}$ (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
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (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

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