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

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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 ultimately afforded $NpCl_3(py)_4$, the only example of a structurally characterized solvated Np(III) halide. The method demonstrates a route to a well-defined Np(III) starting material without the need to employ scarcely available Np metal.

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 non-aqueous 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 non-aqueous 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, non-aqueous 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, non-aqueous Pu(IV) molecules as synthetic precursors are barely developed, with $PuCl_4(DME)_2$ (DME = 1,2-dimethoxyethane) as the only example in the literature.[8] Previous observations have pointed 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 (iodine or bromine addition in organic solvents) 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.[9,12] 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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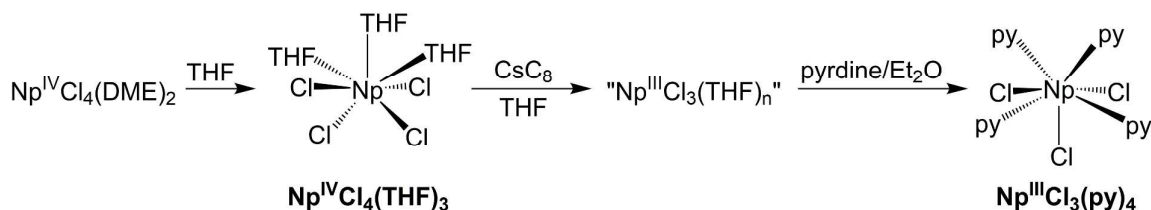
Scheme 1. Synthetic route and crystallization conditions that lead to NpCl$_4$(THF)$_3$ and NpCl$_3$(py)$_4$.

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 ligand binding. 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$_2$Cl$_2$(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 (likely via disproportionation mechanisms). This unusual redox chemistry is counter to examples with other tetravalent

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 environments. 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]

In contrast, 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 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, on the same order as 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$_4$ suspensions in Et$_2$O 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 of our 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 non-aqueous, 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
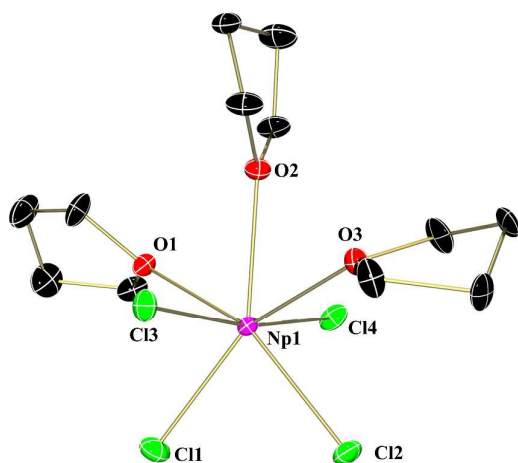

Figure 1. Molecular structure of NpCl$_4$(THF)$_3$ shown with 30% probability ellipsoids. Hydrogen atoms and disorder have been omitted for clarity.

one equivalent of CsC_8 to a stirring solution of $NpCl_4(THF)_3$ in THF caused a color change from salmon to green (Scheme 1). After filtering to remove graphite and CsCl, the solution appeared bright yellow and was subsequently concentrated *in vacuo* to a free-flowing yellow 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 represent 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 suitable for X-ray crystallography (Scheme 1). Refinement of the data revealed that the compound crystallized in a monoclinic C2/*c* space group, and
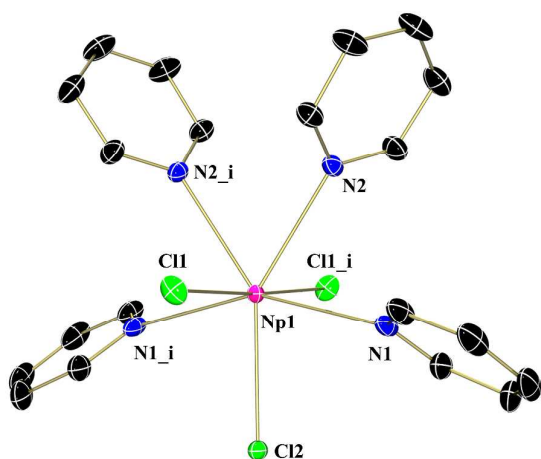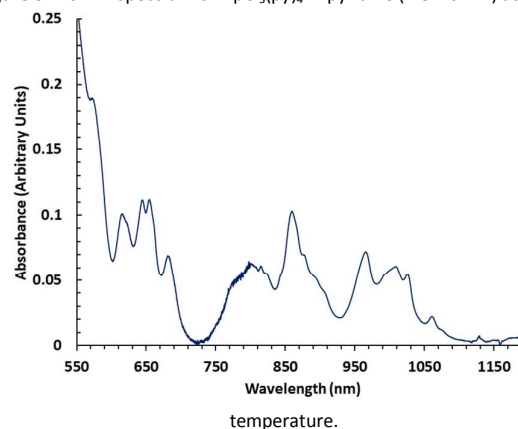
Notably, the structure of $NpCl_3(py)_4$ is monomeric, while the uranium analogue, grown from similar crystallization conditions, is dimeric through two chloride atoms.[20] The Np-Cl distances range from 2.7097(7) to 2.7303(9) Å, slightly longer than the Np(III)-Cl distance of 2.6694(9) Å in $[(L^{Ar})NpCl]$ (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 1.8×10^{-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 (see SI for approximate molar absorptivity values). There are 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 (1.8×10^{-3} M) at ambient

temperature.

Figure 2. Molecular structure of $NpCl_3(py)_4$ shown with 30% probability ellipsoids. Hydrogen atoms and Et_2O lattice molecules 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), and two lattice diethyl ether molecules ($NpCl_3(py)_4 \cdot 2Et_2O$).

In summary, we report solvent exchange and redox properties of the transuranium 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 non-aqueous/inert atmosphere conditions. Reduction of $NpCl_4(THF)_3$ with CsC_8 allowed for the isolation of a yellow powder presumed to be a molecular THF adduct of $NpCl_3$ and expected to be of substantial 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 'starting materials' are not known.
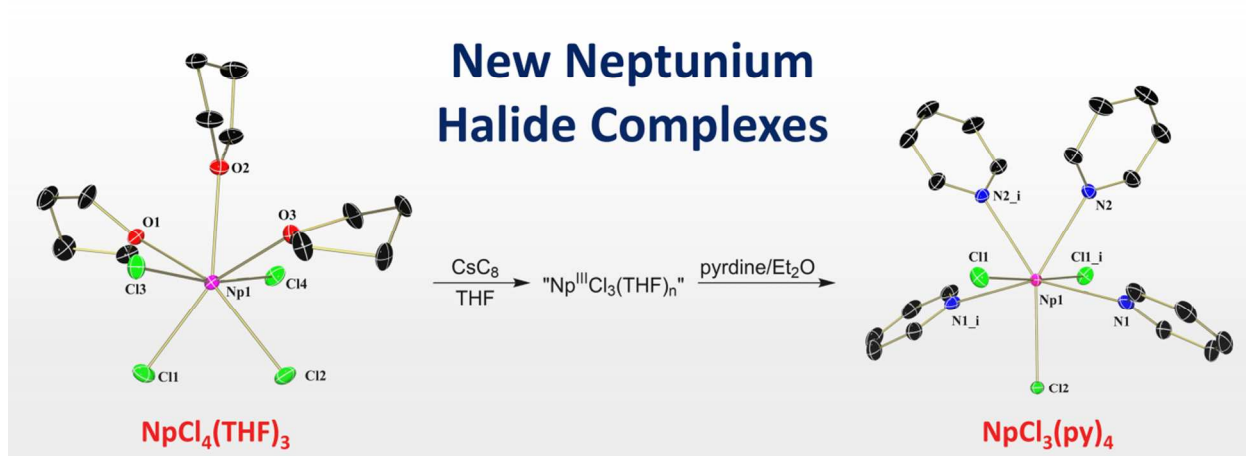
Conflicts of interest

There are no conflicts to declare.

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New Neptunium Halide Complexes

$NpCl_4(THF)_3$ $\xrightarrow[\text{THF}]{CsC_8}$ "$Np^{III}Cl_3(THF)_n$" $\xrightarrow{\text{pyrdine/Et}_2O}$ $NpCl_3(py)_4$

Redox stability of tetravalent Np and Pu in THF is explored, leading to facile access routes into anhydrous Np(III) chemistry.