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Title

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Permalink

https://escholarship.org/uc/item/586266q3

Journal

Angewandte Chemie International Edition, 58(42)

ISSN

1433-7851

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Publication Date

2019-10-14

DOI

10.1002/anie.201906324

Peer reviewed

Synthesis and Utility of Neptunium(III) Hydrocarbyl Complex

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Abstract: *To extend organoactinide chemistry beyond uranium, reported here is the first structurally characterized transuranic hydrocarbyl complex, $Np[\eta^4\text{-}Me_2NC(H)C_6H_5]_3$ (**1**), from reaction of $NpCl_4(DME)_2$ with four equivalents of $K[Me_2NC(H)C_6H_5]$. Unlike the U^{III} species, the neptunium analogue can be used to access other Np^{III} complexes. The reaction of **1** with three equivalents of $HE_2C(2,6\text{-}Mes_2\text{-}C_6H_3)$ $(E = O, S)$ yields $[(2,6\text{-}Mes_2\text{-}C_6H_3)CE_2]_3Np(THF)_2$, maintaining the trivalent oxidation state.*

$\mathbf{S}$ince the synthesis of $Ni(CO)_4$[1] and ferrocene,[2] significant advances in organometallic chemistry continue to be made with respect to metal-based catalysis,[3] materials chemistry,[4] and biomimetic studies.[5] Historically, the Manhattan Project drove the progress of organoactinide chemistry for the potential use of actinide alkyl complexes in separation,[6] and although the focus has changed, organometallic chemistry of the actinides in particular has experienced a renaissance in the past 30 years.[7] This renaissance is especially true of recent advances in low-valent actinide chemistry, that is, divalent and trivalent organoactinide complexes. For example, Th^{2+},[8] U^{2+},[9] Np^{2+},[10] and Pu^{2+},[11] complexes have all been isolated, along with an organometallic americium complex, $(C_5Me_4H)_3Am$.[12] However, because of their lack of thermal stability, actinide alkyls,[13] especially low-valent actinides, are rare.[14] These complexes are of interest for their small-molecule activation,[15] spectroscopic and magnetic properties,[16] as well as starting materials for advancing the fundamental coordination chemistry and reactivity of low-valent actinides.[17] To date, the organometallic chemistry of the actinides, particularly transuranic chemistry, has been dominated by π-ligands such as cyclopentadienyl and other derivatives.[18]

The coordination chemistry of transuranic elements has lagged behind that of thorium and uranium because of the lack of easily accessible starting materials, as well as the associated cost and infrastructure required to obtain and handle these elements. Since transuranic elements are byproducts of irradiating uranium, exploring the chemistry

of these elements is necessary to better understand how to separate the minor actinides from complex matrices when recycling spent nuclear fuel. Despite its relevance in the fuel cycle, the chemistry of neptunium has been largely neglected compared to its neighboring elements, uranium and plutonium.[19]

The organometallic chemistry of neptunium has recently been thoroughly reviewed by Arnold.[20] There are only a few examples of hydrocarbyl complexes with neptunium and all of them tetravalent. For example, only one neptunium(III) alkyl complex, $Np[CH(SiMe_3)_2]_3$, has been claimed, but only characterized by a color change and IR spectroscopy as the compound decomposes rapidly in solution.[21] The reactivity of $(C_5H_5)_3NpCl$ with alkyl lithium reagents has been reported but characterized based on percent Np obtained through α-counting as well as Mössbauer spectroscopy.[22] Additionally, the group of Arnold has suggested these studies warrant further investigation.[20, 23] Further reactivity of $(C_5H_5)_3NpCl$ has been reported to produce alkyl species, $(C_5H_5)_3NpX$, $X =$ Me, Et, CCH and Ph, and characterized by UV-vis-nIR, IR, and EPR spectroscopy as well as magnetic measurements.[24] But, to our knowledge, these studies have not been published. It should be noted that the reactivity of $(C_5H_5)_3NpCl$ with alkyl lithium reagents does form a significant amount of $(C_5H_5)_3Np^{III}$, which is not unexpected given the Np(IV/III) redox couple.[23] Recently, Gaunt and co-workers reported $NpCl_4(DME)_2$,[25] $NpCl_4(THF)_3$, and $NpCl_3(pyridine)_4$,[26] which has replaced $NpI_3(THF)_4$,[27] as a useful neptunium starting materials since neptunium metal is required to prepare $NpI_3(THF)_4$. Here, we report the synthesis of a stable transuranic hydrocarbyl complex, $Np[\eta^4\text{-}Me_2NC(H)C_6H_5]_3$, directly from $NpCl_4(DME)_2$, circumventing the need for an alkali-metal reducing agent.[26] This work is analogous to our recent synthesis of a uranium(III) hydrocarbyl complex, $U[\eta^4\text{-}Me_2NC(H)C_6H_5]_3$, from reaction with UCl_4.[14f] We demonstrate the utility of the Np complex and show that, unlike the uranium analogue, the products maintain the trivalent oxidation state after protonolysis reactions.

The reaction of $NpCl_4(DME)_2$ with four equivalents of $K[Me_2NC(H)C_6H_5]$ produces an immediate color change from pink to black (Scheme 1). The reaction is conducted in THF at $-35\,^{\circ}C$ since the potassium salt will react with THF at room temperature.[28] After 2.5 hours, the solution was filtered through Celite, and the volatiles were removed under vacuum leaving a black powder. The resonances for the Np product in the ^1H NMR spectrum in $[D_8]$toluene range from $\delta = 20.45$ to -62.53 ppm with features in the nIR spectrum consistent with Np^{III} ions having weak 5f–5f transitions.[24] The ^1H NMR spectrum also contained the reductive coupling of two ligands which, because of similar solubilities, could not be separated from the neptunium

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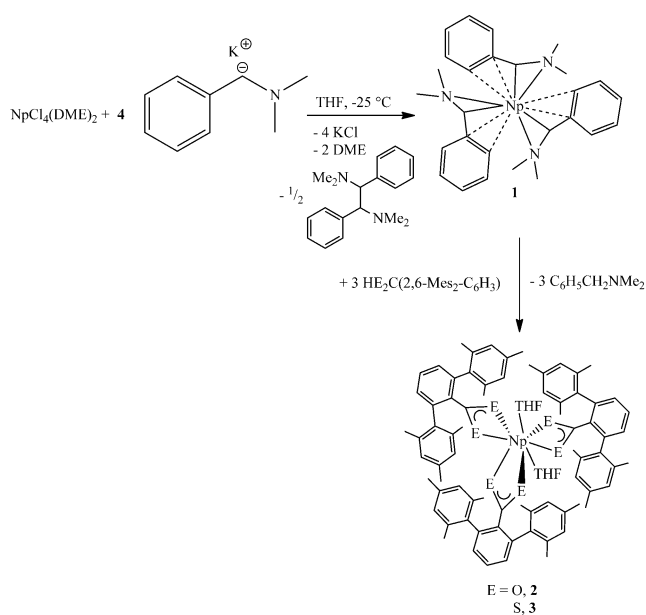
Scheme 1. Synthesis of complexes **1**, **2**, and **3**.

complex. The reduction of Np[IV] to Np[III] is not unexpected given the relative stability of Np[III] compared to U[III]. A variety of elements undergo similar such reductions with alkali metal substrates.[29] Crystals suitable for X-ray crystallographic analysis were obtained from a concentrated toluene solution layered with pentane at −35°C. The crystalline yield was approximately 44%. The structure, Figure 1, revealed Np[η^4-Me$_2$NC(H)C$_6$H$_5$]$_3$ (**1**), which is isostructural to the uranium complex previously reported. The complex **1** is the first structurally characterized neptunium(III) hydrocarbyl complex. Similar ^{1}H NMR resonances are observed in both
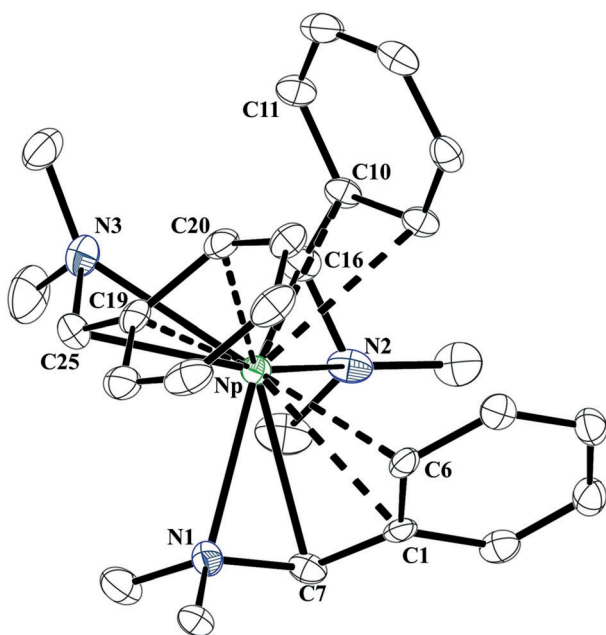
[D$_8$]THF and [D$_8$]toluene, and no decomposition was observed by heating **1** to 50°C in THF overnight, demonstrating its thermal stability.

In **1**, the Np−C(methine) bond distances are 2.592(4) Å (Np−C7), 2.581(4) Å (Np−C16), and 2.574(4) Å (Np−C25), while the Np−N1, Np−N2, and Np−N3 distances are 2.552(3), 2.605(3), and 2.626(3) Å, respectively. The Np−C bond lengths are shorter than those found in Np(C$_5$H$_4$SiMe$_3$)$_3$ as they range from 2.734(6)–2.786(4) Å, but longer compared to the Np-centroid distances of 2.485(2), 2.481(2), and 2.479-(2) Å.[23] The Np−N bond distances in **1** are similar to those observed in Np(C$_5$H$_5$)$_3$(NCMe)$_2$ of 2.665(4) Å.[23] Additionally, Np−C(*ipso*) distances in **1** are 2.787(4) Å (Np−C1), 2.766(4) Å (Np−C10), and 2.769(4) Å (Np−C19), while the Np−C(*ortho*) distances are 2.802(4) Å (Np−C6), 2.813(4) Å (Np−C11), and 2.805(4) Å (Np−C20). These distances are similar to those observed in the uranium analogue,[14f] and much shorter than the agostic interactions seen in Pu[N-(SiMe$_3$)$_2$]$_3$ of 2.968(9) Å.[30] Therefore, we consider this ligand having an η^4 coordination mode with the agostic interactions being a reasonable explanation for the stability of **1**.

As a final comparison, the ionic radii of six-coordinate Np[III] and Ce[III] are both 1.01 Å,[31] hence we can compare the distances in **1** to the Ce[III] analogue,[28] which sits on a pseudo threefold axis of symmetry. However, the Ce−C(methine) bond distances are 2.617(3) Å, which are $\Delta = 0.025(3)$ (Np−C7), 0.036(3) (Np−C16), and 0.043(3) (Np−C25) Å longer than the Np−C(methine) distances in **1**. The closest lanthanide with similar bond distances to **1** is the Nd analogue which has an ionic radius of 0.953 Å. The analogous Nd complex has Nd−C(methine) distances of 2.588(3) Å[28], with the average Np−C(methine) distance in **1** being 2.582(4) Å. This comparison demonstrates the enhanced actinide–ligand bonding that is well-established in 4f versus 5f complexes.[32]

To demonstrate that **1** can be used as a starting material to obtain other trivalent neptunium complexes, the reaction of **1** with three equivalents of HO$_2$C(2,6-Mes$_2$-C$_6$H$_3$)[33] was attempted (Scheme 1). A pale-yellow solution was afforded. Upon crystallization from a concentrated pentane solution at −35°C, X-ray crystallography revealed the structure of the trivalent product, [(2,6-MesC$_6$H$_3$)CO$_2$]$_3$Np(THF)$_2$ (**2**; see the Supporting Information). The crystalline yield was approximately 17%. The UV-vis-nIR spectrum shows an absorption at 400 nm. In addition, features around 1350 nm in nIR region are indicative of Np[III]. The three carboxylate ligands are situated in the equatorial plane while the two THF adducts are in an axial position. The Np−O(carboxylate) bond distances range from 2.435(3)–2.552(3) Å and are longer than the only other Np[III]-alkoxide, K(DME)$_n${(L^{Ar-H})Np-(OCH$_3$)}$_2$ (L^{Ar} = *trans*-calix[2]benzene[2]pyrrole), reported at 2.288(9) Å.[10b] The elongation of the Np−O bond distances in **2** are presumably a result of the steric encumbrance and chelating ability of the terphenyl ligand. The Np−O(THF) bond distances of 2.469(3) and 2.479(3) Å are similar to those Np−O(THF) of 2.487(4), 2.513(5) and 2.538(6) Å in (L^{Ar})Np$_2$Cl$_4$(THF)$_3$.[10b]

To observe whether Np[III] would oxidize upon reaction with a thiocarboxylate in a similar manner as its uranium analogue, the reaction of **1** with HS$_2$C(2,6-Mes$_2$-C$_6$H$_3$) was

Figure 1. Thermal ellipsoid plot of **1** shown at the 50% probability level.[40] The hydrogen atoms have been omitted for clarity.

attempted (Scheme 1). The color instantly turned from black to dark green. The product, $[(2,6\text{-MesC}_6\text{H}_3)\text{CS}_2]_3\text{Np(THF)}_2$ (**3**), was characterized by X-ray crystallography (Figure 2) and obtained in 35% crystalline yield. The complex **3** has a mirror plane on a C_2-axis of symmetry which results in two thiocarboxylate ligands being equivalent. The Np–S distances in **3** range from 2.9286(10)–2.9550(10) Å with the Np–O(THF) distances similar to those in **2** at 2.467(3) Å. Only one other Np[III] complex has been reported with sulfur-based ligands, $[\text{NEt}_4][\text{Np(S}_2\text{CNEt}_2)_4]$. For comparison, its Np–S distances range from 2.86(3)–2.91(3) Å.[34]

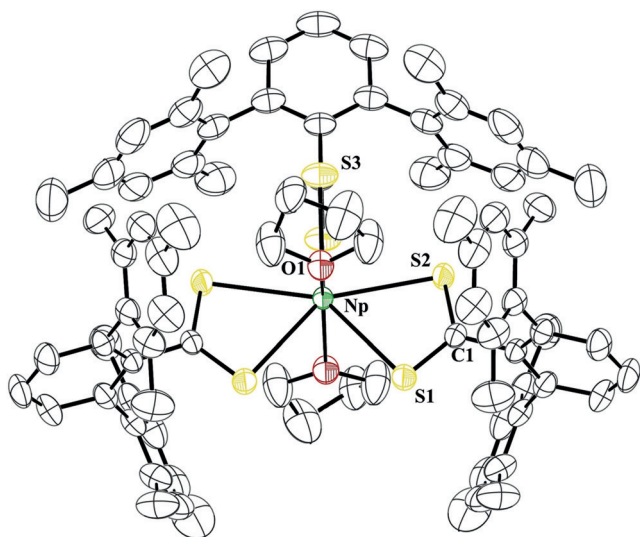**Figure 3.** Variable-temperature magnetic moment of **2** and **3** at 0.1 T.

Figure 2. Thermal ellipsoid of **3** shown at the 50% probability level.[40] The hydrogen atoms have been omitted for clarity.

The magnetism of **2** and **3** were measured to corroborate the assignment of a trivalent oxidation state. Given similar solubilities, the coupled ligand could not be removed from **1** satisfactorily, therefore the magnetism of **1** was not measured. The ground state of Np[III] is $^5I_4$ under Russell Saunders (RS) coupling, and its free ion moment is 2.68 μ_B. Under intermediate coupling, the ground state of Np[III] is $^5I_4$, is primarily (80%) $^5I_4$ and the free ion moment is larger 2.88 μ_B as determined using $\mu_B = g_J[J(J+1)]^{1/2}$ and g_J, for intermediate coupling, 0.644.[35] Unlike U[III] and U[IV], Np[III] and Np[IV] have quite different moments in the ground state, 2.88 μ_B and 3.82 μ_B, respectively, for intermediate coupling. This large difference allows the oxidation states to be determined from the magnetic moment at room temperature if the splitting of the ground-state multiplets is small (less than ≈ 200 cm^{-1}, the value of kT at 300 K). Since the splitting is often larger, especially for tetravalent actinide ions which experience a larger crystal field, the room-temperature magnetic moments do not allow differentiation between Np[III] and Np[IV].

For **3**, the value of χT approaches zero as the temperature approaches zero, which indicates that the ground state is a singlet state (Figure 3). This result is common for a 5f^4 configuration as illustrated by PuO$_2$, which also has a singlet ground state.[36] This situation is also common among U[IV], f^2, complexes. The ground states of both UCl$_6^{2-}$ and UBr$_6^{2-}$ are
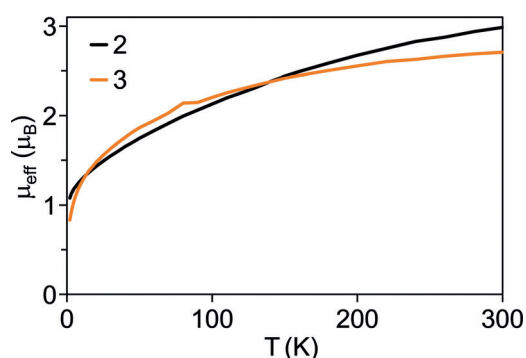
singlets,[37] as is the ground state of $(1,3\text{-}^t\text{Bu}_2\text{C}_5\text{H}_3)_2\text{UCl}_2$.[38] At high temperature, the magnetic moment 2.7 μ_B approaches the free ion moment, and indicates that the splitting of the $^5I_4$ state by the ligands is relatively small. The magnetic susceptibility results support a Np[III] ground state for **3**.

For **2**, the value of χT decreases as T approaches zero, but it does not approach zero. Instead, the low-temperature moment of **2** is 1.1 μ_B. The moment at room temperature is 3 μ_B, which is slightly greater than the free-ion moment of the lowest state of Np[III], but considerably less than the free-ion moment for Np[IV] in intermediate coupling, 3.82 μ_B. The NMR spectra of **2** and **3** support a greater magnetic moment of **3**. The chemical shifts of the mesityl methyl protons are $\delta = 1.99$ ppm and 2.36 ppm for the *ortho* and *para* methyl groups, respectively. In **3**, these resonances are found at $\delta = 2.41$ ppm and 2.14 ppm, respectively. In **2**, the chemical shifts are further from their diamagnetic values at $\delta = 2.56$ ppm and 1.79 ppm. A potential explanation of the difference between the magnetic susceptibilities of **2** and **3**, especially the greater moment of **2**, is the difference the crystal fields of sulfur- and oxygen-based ligands. As illustrated with chromium halides by Burdett,[26] destabilization of metal orbitals is proportional to the ligand ionization potential as well as to the overlap between the metal and ligand orbitals. Because the carboxylate orbitals involved in bonding with Np are more stable than the corresponding thiocarboxylate orbitals, the crystal field of the carboxylate ligand is expected to be greater than that of the thiocarboxylate ligand even if the overlap is similar in both complexes. The obvious effect of this difference is to change the energies of the low-lying excited states created by splitting ground multiplet ($^5I_4$ in RS coupling). As a result, the shapes of the μ_{eff} vs. T curves of **2** and **3** are different. However, the crystal field also mixes excited multiplets (e.g., $^5I_5$ in RS coupling) into the ground state, which can increase the magnetic moment of the complex (the moment of $^5I_5$ state is 4.93 μ_B in RS coupling). The larger magnetic moment of **2** relative to **3** is consistent with the larger crystal field expected for the carboxylate ligand relative to the thiocarboxylate.

In summary, the synthesis and characterization of a neptunium(III) hydrocarbyl complex is reported. This compound is the first structurally and thoroughly characterized hydrocarbyl complex beyond uranium, and has been demonstrated to be a starting material to form further Np[III] complexes. Given the stability of **1**, it is plausible that this

moiety could be applied to other transuranic elements such as plutonium and americium, which have even greater stability of the trivalent oxidation state and for which the starting materials already exist.[25,39] These also represent rare examples of Np[III] complexes for which further chemistry can be explored by utilizing the Np(IV/III) or potentially the Np(V/III) redox couple. These investigations are currently underway.

Acknowledgements

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[40] CCDC 1910635 (**1**), 1910634 (**2**), and 1910633 (**3**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre