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Thorium Mono- and Bis(imido) Complexes Made by Reprotonation of cyclo-Metalated Amides

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Supporting Information

ABSTRACT: Molecules containing actinide—nitrogen multiple bonds are of current interest as simple models for new actinide nitride nuclear fuels, and for their potential for the catalytic activation of inert hydrocarbon C–H bonds. Complexes with up to three uranium—nitrogen double bonds are now being widely studied, yet those with one thorium—nitrogen double bond are rare, and those with two are unknown. A new, simple mono(imido) thorium complex and the first bis(imido) thorium complex, K[Th(═NAr)N⁺], are readily made from insertion reactions (Ar = aryl, N⁺ = N(SiMe₃)₂) into the Th–C bond of the cyclometalated thorium amidic [ThN⁺₂(N(SiMe₃)₂(SiMe₂CH₃))] and K[ThN⁺₂(N(SiMe₃)₂(SiMe₂CH₃))₂]. X-ray and computational structural analyses show a “transition-metal-like” cis-bis(imido) geometry and polarized Th≡N bonds with twice the Wiberg bond order of the formally single Th≡N bond in the same molecule.

Strong and covalent multiple bond formation between actinide cations and oxo groups is a ubiquitous feature of actinide chemistry, most famously represented by the linear O═U═O unit in the uranyl dication [UO₂⁺], in which the ligating atoms strongly donate electron density to the metal through one σ bond and two π bonds in an unreactive and formally triple bond. Studies of multiple bonds between actinide ions and other heteroatoms are still rare but are gaining momentum due to their unique contributions to our understanding of the role of the 5f and other orbitals in covalent bond formation. Imido ligands are strong σ- and π-donors, and uranium imido bonds have a formal order of 3, like uranyl oxos. All known U(VI) uranyl complexes contain trans-dioxo ions, and nearly 90% of U(VI) bis(imido) complexes have a close to linear (≈150°) geometry; examples of cis- and trans-U(VI) bis(imido) complexes, respectively are (Cp*)₂U(═NR)₂ (A in Figure 1) and the landmark, linear uranyl analogue [U(═NR)₂L₂(THF)] (B).⁴ Meanwhile, the majority (ca. 95%) of the numerous transition metal bis(imido) complexes exhibit cis geometries (e.g., C in Figure 1).

Recent years have seen a great increase in the number and variety of terminal imido uranium complexes, including bis-imido and most recently U(VI) tris(imido) structures (D in Figure 1). Their bonding has been studied in terms of proving molecular analogues of actinide nitride nuclear fuels, and their reactivities have been studied in the search for catalytic properties which might differ from those of the d-block complexes.⁷ An intramolecular ligand C=H bond addition reaction was initiated by diazoalkane binding to a U(VI)=N bond in the complex (C₅Me₅)₂U(═NC₆H₄Bu)₂(N₂C₅H₄), the strong donation of the N(2p) orbitals and involvement of the uranium 5f orbitals is not conducive to the most desirable intermolecular hydrocarbon C–H bond addition chemistry, for which the more polar transition metal M≡N bonds have been celebrated.⁹ Only four terminal thorium imido complexes have been reported, all of which are supported by the bulky, clam-shaped bis(cyclopentadienyl) co-ligand set (E in Figure 1).¹⁰ Early reports on the small-molecule activation reactivity of E include silane Si–H bond cleavage chemistry.¹¹ This supports the suggestion of more d-block-like behavior of thorium (cf. uranium), which is afforded by its ground-state [Rn]⁵⁺s² configuration, and a therefore greater potential for the reactivity of the Th≡NR group. No bis(imido) complexes have been reported to date, which could be due to their anticipated higher reactivity compared to the uranium analogues (calculations on the model [(C₅H₅)₂Th(═NPh)₂]²⁻ ion find much weaker metal–nitrogen bonding than in the uranium complex),¹² and also to the difficulty in stabilizing low coordination numbers at the large Th⁴⁺ center.¹³

Given that A has no equivalent in transition-metal chemistry, we were interested in thorium imido complexes of monodentate,
Scheme 1. Synthetic Routes to the Bis(metallacyclic) Amido, and Mono- and Bis(imido) Thorium(IV) Complexes

```
\[
\begin{align*}
N^" &= N(SiMe_3) \\
Si &= SiMe_3
\end{align*}
\]
```

Two syntheses of \([K(S)\][Th(N(Si')2(SiMe2CH2)2)]2N\]^+\) (1), and the conversion of the mono- and bis(metallacycles) into the mono- and bis(imido) complexes \([K(S)\][Th(NDipp)N\]^+\) (2) and \([K_2(S)\]3b, \([Th(N(Si')2(SiMe2CH2)2)]2N\]^+\) (3), respectively. For 1a, x = 0; for 1b, S = 18-c-6, x = 1; for 1c, S = DME, x = 1; for 2a, x = 0; for 2b, S = 18-c-6, x = 1; for 3a, S = THF, x = 2; for 3b, S = 18-c-6, x = 1; for 3c, S = 18-c-6, x = 2. 18-c-6 = C12H18O8 crown ether.

 monoanionic ligands which would not be sterically protected or geometrically directed by the "clam-shell" configuration of the bis(cyclopentadienyl) framework. Herein we report a new, straightforward route to amido-imido ThIV complexes and the first thorium bis(imido) complex. We also discuss their bonding and geometries with the support of density functional theory (DFT) calculations.

Treatment of a THF solution of the thorium metallacycle Th[N(Si')2(SiMe2CH2)2]N^+ (A, where N" = N(SiMe2CH2)2, Si = SiMe3) with 1 equiv of KN affords the bis(metallacycle) \([K(S)\][Th(N(Si')2(SiMe2CH2)2)]2N\]^+ (1) as a colorless solid (Scheme 1). It can be also made from ThCl4(DME), and 5 equiv of KN in toluene and is isolable solvent-free in 70% yield (1a) or as a variety of solvates, depending on the precursor and workup procedure, including crown ether, \([K(18-c-6)][ThN^+(N(Si')2(SiMe2CH2)2)]\) (1b), and DME, \([K(18-c-6)][ThN^+(N(Si')2(SiMe2CH2)2)]\) (1c) (18-c-6 = 18-crown-6, C12H18O8). This "ate" complex is the direct analogue of the UIV complex \([K(THF)][U(N(Si')2(SiMe2CH2)2)]2N\]^+ reported by Ephrath-Khineh. At room temperature, NMR spectroscopy in CD2Cl2/THF solution shows the diastereotopic relationship of the metallacyclic groups in 1. In spectra of 1a, the CH2 protons are observed as two broad resonances at 0.04 (W1/2 ~ 47 Hz) and -0.37 (W1/2 ~ 42 Hz) ppm, which coalesce at 343 K; the Si(CH2)3 hydrogens are observed as a single broad resonance at 0.49 ppm (W1/2 ~ 59 Hz, 12 H). The 13C{1H} NMR spectrum shows a broad resonance for the Th–CH2 group at 53.4 ppm (the corresponding resonance in A is 68.8 ppm). Two broad resonances at 6.8 and 8.7 ppm are assigned as the diastereotopic Si(CH2)3 carbons. The 29Si-INEPT spectrum shows the three anticipated resonances at \(\delta = -28.9, -16.9,\) and -11.8, which compare closely with \(\delta = -32.9, -12.1,\) and -9.4 for A. Complex 1 does not react with further KN" in our hands.

Treatment of A with KNHDipp (Dipp = 2,6−Pr2C6H3) in C6H6/THF or THF provides straightforward access to the colorless crystalline thorium imide \([K(S)\][Th(NDipp)N\]^+\) (2, Scheme 1), isolable as a variety of solvates, depending on the workup procedure. For example, from THF solution unsolvated 2a (S = 0) is isolated in quantitative yield, but addition of crown ether (18-c-6) and a small quantity of THF (10% by volume) to the benzene reaction mixture affords the separated ion-pair \([K(18-c-6)][Th(NDipp)N\]^+\) (2b). Complex 2 is highly oxygen and moisture sensitive but thermally stable for at least 14 days in a refluxing toluene/THF solution (ca. 10% THF). NMR and X-ray diffraction (XRD) studies (see below) of 2 confirm the addition of the [HNDipp] group across the Th–C bond to form the Th=NDipp aryl imido complex. No NH resonance is observable in the spectra, and in the aliphatic region a lone singlet at \(\delta 0.28\) (sH4) confirms the equivalence of the two original silylamide ligands and regenerated \(N^+\) amido ligand. Finally, 29Si-NMR spectra show a single silicon environment with a chemical shift of -11.2 ppm. A number of other arylimido analogues of 2 were also made and are discussed in the Supporting Information (SI).

Analogously, treatment of 1a with 2 equiv of KNHDipp in a C6H6/THF mixture (ca. 5:1 ratio) yields the first bis(imido) complex of thorium, \([K_2(S)\][Th(NDipp)2]2N\]^+\) (3), as a colorless crystalline solid in essentially quantitative yield (Scheme 1). Again, different solvated forms can be isolated, but the simple THF adduct (3a, with S = THF, x = 2, 85% yield) most readily forms single crystals suitable for XRD studies (see Figure 2). The mono- and bis-18-c-6 analogues 3b and 3c are described in the SI, section IVc. The complex is mononuclear in solution as well as in the solid state: \(^1\)H NMR spectra of 3a in CD3OD solvated with a few drops of THF, contain a singlet at \(\delta 0.26\) (36H), demonstrating a single silylamide environment. \(^1\)H DOSY NMR spectroscopic experiments (SI, section V) show the hydrodynamic radius of 3a (7.1 Å) to be similar to that of 2a (6.9 Å), suggesting that 3 remains monomeric in solution. The highest mass peak in the electron ionization mass spectrum of 3c is at 1509.2 m/z, corresponding to the ion-pair \([K(18-c-6)][Th(NDipp)2]2N\]^+\). The MALDI spectrum clearly shows a molecular ion at 901.5 m/z, corresponding to \([Th(NDipp)2]2N\)^+\). No ion with higher mass was observed by either method.

Once isolated, 3 is stable for several days in solution, but if stored in contact with the soluble KN" byproduct, over 8 h at room temperature solutions begin to degrade to multiple products, as determined by \(^1\)H NMR spectroscopy. Other bis(imido) analogues were also targeted, but none was as stable as 3; see SI, section IV for details.

X-ray-quality crystals of 1c were grown by slow cooling of the hexane filtrate of a sample made from ThCl4(DME), X-ray-quality crystals of 2b were grown by slow cooling of a CD3OD/THF solution, while single crystals of 3a were grown by slow diffusion of hexane into a C6H6/THF solution. The molecular structure of 1c (Figure 2a) confirms the metatation of both amido ligands. Although the solid-state structure of A is not known, the two Th–C bonds of 2.562(S) and 2.576(5) Å fall within the expected range for single Th–C bonds (2.4–2.8 Å).

The molecular structure of 2b (Figure 2b) shows a tetrahedral thorium environment with a Th1–N1 imido bond length of 2.072(3) Å that is significantly shorter than a single Th–N amido bond (range 2.2–2.4 Å for thorium dialkylamides) but is one of the longest Th–N imido bonds observed to date. The four reported terminal thorium imido complexes E all contain two cyclopentadienyl co-ligands, either \([\{(C5Me5)2\}]^{10\text{th}}\) or
both the nitrogen and ipso-aryl carbon atoms of each imido group, a feature observed previously in related uranium systems.7)

The other, K2A/K3 (disordered over two sites), is weakly bound in an approximately bis(arene) sandwich-type geometry through coordination to the imido aryl rings of adjacent molecules, resulting in the formation of one-dimensional chains in the solid state.

The mono- (2) and bis(imido) (3) structures were studied using theoretical methods (DFT) on model compounds 2’ and 3’, with potassium counterions omitted (see SI, section VIII for details and further analysis of the data). The computational method reproduced the geometry of 2 and 3 very well, indicating the suitability of the chosen method. Analysis of the bonding in 2, using NBO, indicates double-bond character in the Th=Nimido bond in 2 at the second-order donor–acceptor level, with a polarized σ bond and an ionic π interaction involving donation from the nitrogen 2p orbital toward an empty 6d/5f hybrid orbital on Th. There is a greater polarization than the bonding in the recently reported Th=O analogue, as expected,17 and a greater d orbital involvement than f, in line with previous studies by us.18

In 3’, these double bonds can be described as a polarized covalent σ bond (90% 2p N; 10% 6d(65)-5f(35) Th) and an ionic π interaction involving donation from the nitrogen 2p orbital toward an empty 6d orbital on Th (second-order NBO, 44.2 kcal/mol). Figure 3 shows the calculated HOMO and HOMO−1 orbitals and a greater d orbital involvement than f, in line with previous studies by us.18

Figure 3. Calculated π Th=Nimido interaction in 3’. (a) HOMO and (b) HOMO−1 orbitals shown at the default isosurface value of 0.025. (c) Schematic of the thorium imido bonding.

[(C₅H₅)(NBu)₂]⁻.11a It is likely that the Th−N lengthening in 2 reflects the electron richness of the metal center due to both the normal negative charge on the Th⁺ center and the presence of electron-donating silylamide ligands, each of which has been shown to result in a measurable M=N lengthening in d-block analogues.16

The structure of 3a (Figure 2c) shows a pseudo-tetrahedral thorium environment and a cis arrangement of the two imido ligands with a N4−Th1−N3 bond angle of 97.34(12)°, close to that which has been theoretically predicted (see below). The two thorium imido Th=N bonds (both 2.165(3) Å) are longer than that in 2b (2.072(3) Å) but significantly shorter than the thorium amido Th=N bonds (Th1−N1, 2.448(3) Å and Th1−N2, 2.474(3) Å). Both Th=Nimido−CDiipp angles are also very close to linear, as would be anticipated for a Th=N bond order of 2 or 3 (C13−N3−Th1, 169.1(3)° and C25−N4−Th, 117.4(3)°).

One of the two potassium counter-cations (K1) occupies the gap between the two imido groups, with relatively close contacts to

[(C₅H₅)₂SiMe₂CH₂]⁻N,[(K(DME))][Th(N(SiMe₂CH₂)₂)₂N]⁺ (1c), (b) [K(18-c-6)][Th(═NDipp)₂N]⁺ (2b), and (c) [K(THF)]₂[Th(═NDipp)₂N]⁺ (3a). Displacement ellipsoid plots in all structures are drawn with 50% ellipsoid probability for all atoms except for peripheral C atoms and, in (b), the Dipp carbons. All hydrogen atoms other than those on the two metalated carbons in (a) are omitted for clarity. Selected distances (Å) and angles (deg): (a) Th1−N2, 2.352(3), Th1−N1, 2.363(4), Th1−N3, 2.381(4), Th1−C6, 2.562(5), Th1−C10, 2.576(5), N2−Th1−N1, 138.14(14), N2−Th1−N3, 109.52(13), N1−Th1−N3, 112.14(13), N2−Th1−C6, 86.24(14), N3−Th1−C6, 123.40(16), N2−Th1−C10, 67.93(14), N1−Th1−C10, 89.37(14), N2−Th1−C6, 86.24(14), N3−Th1−C10, 127.55(15), N1−Th1−C6, 67.85(15), C6−Th1−C10, 108.91(18); (b) Th1−N1, 2.072(3), Th1−N2, 2.424(3), Th1−N3, 2.449(3), Th1−N4, 2.406(3), N1−Th1−N4, 103.56(11), N1−Th1−N2, 98.57(12), N4−Th1−N2, 122.64(11), N1−Th1−N3, 115.69(12), N4−Th1−N3, 103.73(10), N2−Th1−N3, 112.93(11), C1−N1−Th1, 172.0(3); (c) Th1−N1, 2.165(3), Th1−N4, 2.165(3), Th1−N1, 2.448(3), Th1−N2, 2.474(3), K1−N4, 2.840(3), K1−C25, 3.086(3), K2A−C25, 3.130(4), K2A−Ct1, 2.851, N1−Th1−N4, 107.08(11), N1−Th1−N2, 111.73(11), N4−Th1−N2, 112.60(11), N1−Th1−N3, 115.33(11), N4−Th1−N3, 97.34(12), N2−Th1−N3, 108.70(11), C13−N3−Th1, 169.1(3), C25−N4−Th, 171.4(3).

The structure of 3a (Figure 2c) shows a pseudo-tetrahedral thorium environment and a cis arrangement of the two imido ligands with a N4−Th1−N3 bond angle of 97.34(12)°, close to that which has been theoretically predicted (see below). The two thorium imido Th=N bonds (both 2.165(3) Å) are longer than that in 2b (2.072(3) Å) but significantly shorter than the thorium amido Th=N bonds (Th1−N1, 2.448(3) Å and Th1−N2, 2.474(3) Å). Both Th=Nimido−CDiipp angles are also very close to linear, as would be anticipated for a Th=N bond order of 2 or 3 (C13−N3−Th1, 169.1(3)° and C25−N4−Th, 117.4(3)°).
thorium complex, \([\text{K}_2(\text{S}_2)(\text{Th}(\text{NDipp})_2\text{N}^\text{+}])\) (3), are both readily accessible from the simple, well-known thorium amido-
methallacycle, \(\text{Th}([\text{N(Si)}(\text{SiMe}_2\text{CH}_3)]\text{N}^\text{+})(\text{A})\) and a doubly meta
talated analogue, \([\text{K}][\text{Th}([\text{N(Si)(SiMe}_2\text{CH}_3)]\text{N}^\text{+})]\) (1). These are the first thorium-imido-containing complexes to be isolated
without the support of the sterically constraining, clam-shell-
shaped bis(cyclopentadienyl) ligand set. The Th=N bonds are relatively long in both 2 and 3, presumably reflecting the electron-
richness of the metal center compared to those in the bis(cyclopentadienyl)-ligated set. The Th=N bonds in the same molecule, suggesting a much more polar
DFT (Wiberg) methods are twice the value of the single Th=
N bond than compared with uranium analogues, more like
and Dr Christos Apostolidis, Institute of Transuranic Elements,
and France, Humboldt Foundation, CINES, and CalMip.

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This paper was published ASAP on August 12, 2015. Due to a production error, Figures 1 and 2 have been corrected. The revised version was re-posted on August 14, 2015.