Uranium Complexes

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Investigation of Uranium Tris(imido) Complexes: Synthesis, Characterization, and Reduction Chemistry of [U(NDIPP)$_3$(thf)$_3$]**

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Abstract: *Addition of KC_8 to trivalent [$UI_3(thf)_4$] in the presence of three equivalents of 2,6-diisopropylphenylazide (N_3DIPP) results in the formation of the hexavalent uranium tris(imido) complex [U(NDIPP)$_3$(thf)$_3$] (**1**) through a facile, single-step synthesis. The X-ray crystal structure shows an octahedral complex that adopts a facial orientation of the imido substituents. This structural trend is maintained during the single-electron reduction of **1** to form dimeric [U(NDIPP)$_3${K(Et$_2$O)}]$_2$ (**2**). Variable-temperature/field magnetization studies of **2** show two independent U^V $5f^1$ centers, with no antiferromagnetic coupling present. Characterization of these complexes was accomplished using single-crystal X-ray diffraction, variable-temperature ^{1}H NMR spectroscopy, as well as IR and UV/Vis absorption spectroscopic studies.*

Metal imido moieties are synthesized in a variety of ways[1] and play key roles in many organometallic processes, including olefin polymerization,[2] alkyne hydrogenation,[3] azide hydrogenation,[4,5] C$-$H bond activation,[6] and group-transfer processes.[4,7] Although low-valent mono(imido) species have been heavily studied, relatively little is known about more oxidized species bearing two or three imido substituents. Most rare is the tris(imido) family, whose first monomeric entry, [Os(NDIPP)$_3$] (DIPP = 2,6-diisopropylphenyl), was reported by Schrock et al. in 1990.[8] Since then, examples of these types of species have been isolated for Groups IV,[9] V,[10] VI,[11] and VII[12,13] and feature oxidation states of +4 or higher. A uranium analogue has only recently been reported,[14] which is surprising given the important role of its oxygen analogue, UO_3, in nuclear fuel generation and processing.[15]

Uranium complexes bearing three multiply bonded substituents are quite rare. Progress has been made towards this goal using the phosphine-supported carbene ligands, [C(Ph$_2$PE)$_2$]. Both Ephritikhine et al. (E = S)[16] and Liddle and co-workers (E = NSiMe$_3$)[17] describe three formal multiple bonds to U^{VI} centers for [UO$_2$(C(Ph$_2$PS)$_2$)(py)$_2$] (py = pyridine) and [U(C(Ph$_2$PNSiMe$_3$)$_2$)(NMes)(O)(DMAP)$_2$] (DMAP = 4-dimethylaminopyridine), respectively, with charge delocalization across the phosphine backbone and the carbon atom, generating a U-C interaction intermediate between a single and double bond. Arnold et al. have reported pacman-shaped uranyl complexes of the Schiff base polypyrrolic macrocycle L with formula [(R$_3$SiOUO)$_2$(L)], where one oxo ligand is capped by a silyl group and the other by a second uranium center, slightly decreasing the multiple bond order.[18]

We recently made an entry into this category with the synthesis and characterization of the first uranium tris(imido) complexes, [(^{Mes}PDI^{Me})U(NAr)$_3$] (^{Mes}PDI^{Me} = 2,6-(Mes-N=CMe)$_2$C$_5$H$_3$N; Ar = Mes or DIPP), synthesized through arylazide reduction.[14] These unprecedented U^{VI}, f^0 tris(imido) complexes result from a twelve-electron transfer from the highly reduced [(^{Mes}PDI^{Me})U(thf)]$_2$ dimer, with eight electrons derived from the redox-active ^{Mes}PDI^{Me} ligands and four uranium f electrons. Crystallographic data showed [(^{Mes}PDI^{Me})U(NAr)$_3$] displayed an inverse *trans* influence (ITI),[19,20] although less so than Boncella's uranyl analogue *trans*-[UI$_2$(NPh)$_2$(thf)$_3$],[20] as highlighted by a computational analysis that showed *trans*-bond weakening as a result of the competition with the equatorial imido substituent for f-orbital participation. These exciting results prompted further investigation to determine if the pyridine diimine ligand is essential in the generation or support of the three U=N multiple bonds. Herein, we report a new THF-supported uranium tris(imido) species that lacks a traditional ancillary ligand along with its subsequent reduction chemistry.

Treatment of a stirred solution of blue [UI$_3$(thf)$_4$] in THF with N$_3$DIPP (3 equiv) followed by slow addition of potassium graphite (KC$_8$; 3 equiv) over approximately 20 min resulted in vigorous effervescence of dinitrogen (Figure 1 A). Workup furnished a brown solid presumed to be [U(NDIPP)$_3$] in excellent yield (91 %), which was recrystallized from diethyl ether/pentane.[19] Notably, [UI$_3$(thf)$_4$] and N$_3$DIPP do not react at ambient temperature in the absence of KC$_8$ as observed by ^{1}H NMR spectroscopy. The imido substituents were confirmed by a sharp band at 1240 cm^{-1} and a smaller shoulder at 1205 cm^{-1} in the infrared spectrum (see Figure S10/S11 in the Supporting Information), consistent with a U=N$-$C moiety. The energy of this absorption is similar to that for *trans*-[UI$_2$(NPh)$_2$(thf)$_3$] (1270 cm^{-1})[20] and calculated for *cis*-[UI$_2$(NPh)$_2$(thf)$_3$] (1260–1280 cm^{-1}).[21] [U-

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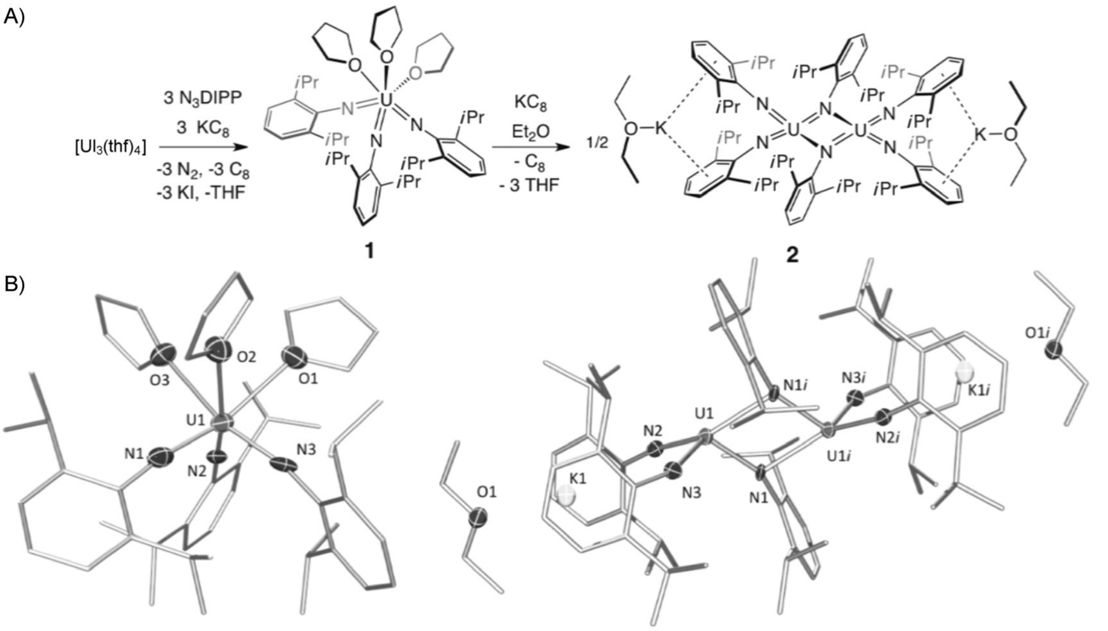

Figure 1. A) Reaction scheme showing the formation of complexes **1** and **2**. B) Molecular structures of **1** (left) and **2** (right). Hydrogen atoms and outer sphere solvent molecules have been excluded for clarity. Carbon atoms have been depicted as a wire frame to properly show the molecular geometry about the metal centers. Selected bond lengths [Å] and angles [°] for **1**: U1−N1 1.986(14), U1−N2 2.000(16), U1−N3 2.010(15), U1−O1 2.595(13), U1−O2 2.616(13), U1−O3 2.618(12); N1-U1-N2 99.7(5), N1-U1-N3 99.8(5), N2-U1-N3 101.6(5). For **2**: U1−N1 2.122(7), U1−N2 2.036(8), U1−N3 2.085(8), U1−N1*i* 2.371(6); N1-U1-N2 100.6(3), N1-U1-N3 115.3(3), N2-U1-N3 96.4(3), N2-U1-N1*i* 146.2(3), U1-N1-U1*i* 106.2(3).

$(NDIPP)_3]$ is stable at room temperature for days in the solid state under an inert atmosphere.

^{1}H NMR spectroscopic characterization (23 °C, $[D_6]$benzene) of $[U(NDIPP)_3]$ shows a diamagnetic C_{3v}-symmetric complex, with four resonance signals present for the DIPP substituents (Figure S1). Doublets at $\delta = 1.63$ (36 H) and 7.98 ppm (6 H) are assignable to the *i*Pr-CH_3 and *m*-aryl C*H* protons, respectively. The *i*Pr-C*H* resonance (6 H) is a septet appearing at $\delta = 5.40$ ppm, whereas the triplet for the *p*-C*H* proton is shifted to $\delta = 4.63$ ppm. Extreme shifts for the imido protons as compared to the azide diamagnetic reference values have been previously reported for $[(^{Mes}PDI^{Me})U(NDIPP)_3]$ and is likely the result of temperature-independent paramagnetism (TIP), as has been measured for uranyl and U^{VI} *cis*-bis(imido) complexes.[22,23] Further confirmation of the identity of $[U(NDIPP)_3]$ was accomplished by addition of one equivalent of the $^{Mes}PDI^{Me}$ ligand which resulted in quantitative formation of $[(^{Mes}PDI^{Me})U(NDIPP)_3]$, as detected by ^{1}H NMR spectroscopy. Also noted in the ^{1}H NMR spectrum of this reaction was the release of free THF (by integration of the area under the resonance signals, circa 2.75 equiv were released; Figure S8).

No signals for coordinated THF molecules were detected in the room temperature ^{1}H NMR spectrum of $[U(NDIPP)_3]$, thus variable-temperature studies were performed to confirm their presence. Cooling a $[D_8]$toluene solution of $[U(NDIPP)_3]$ to −40 °C resolved two resonance signals at $\delta =$ 4.31 and 1.36 ppm (Figure S3), attributed to three coordinated THF molecules for $[U(NDIPP)_3(thf)_3]$ (**1**). Additionally, the chemical shifts for **1** are found to be temperature independent from RT to −40 °C.

To determine the geometry of **1**, dark-brown crystals suitable for X-ray crystallography were grown from a concentrated THF/*n*-hexane (2:5) solution. Refinement of the data revealed a distorted octahedral uranium center with three imido ligands and three coordinated THF molecules in a facial orientation, consistent with the solution-phase characterization (Figure 1B, Table S1). The U−N$_{imido}$ distances of 1.968(14), 2.000(16), and 2.010(15) Å for U1−N1, U1−N2, and U1−N3, respectively, are on the order of those previously characterized for uranium(VI) complexes.[22,24] The N-U-N angles vary from 99.7 to 101.6°, and are reminiscent of *cis*-bis(imido) complexes, which have N-U-N angles of 96.6(8)° ($[Cp_2{*}U(NAd)_2]$),[25] 98.7(4)° ($[Cp_2{*}U(NPh)_2]$),[22] and 103.4(3)° ($[Cp_2U(NtBu)_2]$).[24] Each thf ligand is *trans* to an imido ligand, featuring N-U-O bond angles ranging from 162.2 to 165.9°. The coordination geometry of **1** was surprising given that $[(^{Mes}PDI^{Me})U(NAr)_3]$ shows a meridional orientation with C_{2V} symmetry. The complex *mer*-$[(^{Mes}PDI^{Me})U(NAr)_3]$ is likely preferred due to the presence of the planar $^{Mes}PDI^{Me}$ ligand and the *trans* orientation of the multiply bonded substituents. The *cis* multiply bonded ligands in **1** are reminiscent of those in $[(R_3SiOUO)_2(L)]$, where the pacman ligand enforces a uranyl dimer with *cis*-oxo ligands (O-U-O angle of 73.3(2)°).[18]

Considering the arrangement of only the three imido substituents, the pyramidal geometry observed for **1** is similar to the molybdenum and tungsten tris(imido) complexes, $[MCl(NDIPP)_3]^-$ and $[M(PMe_3)NDIPP)_3]$ (M = Mo, W)[11,28] as well as the majority of $[M(NR)_3]$ complexes (M = Ti,[9] Cr,[26] Mn,[27] Tc,[12] Re[12]). This geometry is different with respect to $[Os(NDIPP)_3]$[8] and $[Re(NDIPP)_3]^{-}$[28] which show trigonal planar geometries as a result of occupation of the d_{z^2} orbital.

Electrochemical analysis of **1** showed a quasireversible reduction wave at −2.14 V versus ferrocene (Fc), suggesting formation of a U^{V} species (Figure S17). Chemical reduction of **1** was accomplished using a single equivalent of KC_8. Following workup, a brown powder assigned as $[K(Et_2O)]_2[U(NDIPP)_3]_2$ (**2**) was isolated (86 %). Analysis of **2** by ^{1}H NMR spectroscopy showed a paramagnetically broadened and shifted spectrum with eleven resonance signals, suggestive of C_{2v} symmetry (Figure S7). Three signals ($\delta = 11.11$, -5.56, and -16.81 ppm) for the iPr-CH_3 protons are substantially broadened with respect to the rest of the spectrum, and two signals for coordinated diethyl ether molecules are noted. The infrared spectrum of **2** shows an intense characteristic absorption at 1237 cm^{-1} with a small shoulder at 1255 cm^{-1} in accord with presence of inequivalent U=N−C moieties (Figure S10/S11).

Compound **2** was also analyzed by X-ray diffraction, using dark-brown crystals grown from a concentrated diethyl ether/pentane (2:1) mixture at −35 °C. Refinement of the data revealed a dimeric uranium tris(imido) dianion (Figure 1 B, Table S2) where two of the imido aryl rings are coordinated in an η^3-mode to two potassium cations. Diethyl ether molecules complete the coordination sphere of these cations. This molecular structure mirrors the asymmetry seen in the ^{1}H NMR spectrum, supporting that **2** remains dimeric in solution. As expected for the larger U^{V} ion, the three $U-N_{imido}$ bonds are longer as compared to **1**, with distances of 2.122(7) (U−N1), 2.036(8) (U−N2), and 2.085(8) (U−N3) Å. Examination of the monomeric unit shows a three-coordinate, pseudo-trigonal pyramidal uranium with three imido substituents *cis* to each other displaying N−U−N bond angles ranging from 96.4° to 115.3°, reminiscent of $[U\{N(SiMe_3)_2\}_3]$.[29]

The dimeric U_2N_2 core is asymmetric with a center of inversion displaying a long bridging U1−N1 distance of 2.371(6) Å that compares well with the analogous U−N bonds for the U^{V} *trans*-bis(imido) complex $[U(NtBu)_2(I)(tBu_2bpy)]_2$.[30] The bond angles in **2** are notable in that there is no true *trans*-imido interaction, as the nearest to linear (N2−U1−N1*i*) has a significantly more acute angle of 142.3(3)°. This is in striking contrast to $[(^{Mes}PDI^{Me})U(NDIPP)_3]$ and $[U(NtBu)_2(I)(tBu_2bpy)]_2$ where *trans* imido substituents display respective angles of 170.6(2)°[31] and 166.6(2)°. Furthermore, the bridging imido substituents in **2** have a U1-N1-C10 angle of 155.5(5)°, larger than that detected for the analogous bridging imido unit in $[U(NtBu)_2(I)(tBu_2bpy)]_2$ (130.5(4)°).

Compounds **1** and **2** were found to be stable for days in $[D_6]$benzene solutions as indicated by aging experiments that were monitored by ^{1}H NMR spectroscopy (Figures S15 and S16, respectively). The single-electron reduction of **1** could be chemically reversed upon the addition of one equivalent of I_2 to **2**, which produced **1** quantitatively. Additionally, **1** is seen to react with I_2 as well, resulting in the formation of $[UI_2(NDIPP)_2(thf)_3]$[32] along with extrusion of half an equivalent of DIPPN=NDIPP, as determined by ^{1}H NMR spectroscopy (Figure S18).

The electronic structures of **1** and **2** were probed using electronic absorption spectroscopy by acquiring data for each complex from $\lambda = 350$–2100 nm (Figure S9). Both complexes display similar absorption profiles with a gradual increase in molar absorptivity approaching higher energies, reminiscent of $[(^{Mes}PDI^{Me})U(NAr)_3]$. The absorptions throughout the visible region are likely due to a combination of $\pi(U{=}N)\rightarrow\pi^*(U{=}N)$ and $\pi(U{=}N)\rightarrow U(5f)$ transitions, as for the absorption profile of the U^{VI} bis(imido) family.[21] The spectrum for compound **2** shows a weak but sharp 5f–5f transition at $\lambda = 1658$ nm, characteristic of U^{V}-centered $5f^1$ ions.[14]

To evaluate the magnetic properties of **2**, temperature-dependent magnetic data were collected on solid samples between 2–300 K. The χT versus T data (χ = magnetic susceptibility; Figure 2 A) achieved a value of 1.46 emu K mol^{-1} ($\mu_{eff} = 3.42\ \mu_B$; μ_{eff} = effective magnetic moment) at 300 K, which was nearly identical to the value of 1.48 emu K mol^{-1} ($\mu_{eff} = 3.44\ \mu_B$) reported for $[U(NtBu)_2(I)(tBu_2bpy)]_2$.[30] The large χT value was attributed to TIP and corroborates the positive slope of the linear χT versus T (high temperature) regime.[33] An estimate of the $\chi_{TIP} = 1.5 \times 10^{-3}$ emu mol^{-1} was obtained from a linear fit of the slope in χT versus T in the 140–300 K range.

Antiferromagnetic (AF) coupling between $5f^1$ centers was reported between the two $^2F_{5/2}$ U^{V} centers in $[U(NtBu)_2(I)(tBu_2bpy)]_2$ in which a maximum in the χ versus T data at 13 K was observed. This was ascribed to π bonding between two *trans*-$[U(=NtBu)_2]^+$ moieties, which allowed for magnetic communication between the $5f^1$ centers. No evidence for AF coupling was evident for **2** from the χ versus T data (Figure 2 B), despite the short U−U distance at 3.5968(6) Å in the solid state. It is postulated that the absence of *trans*-

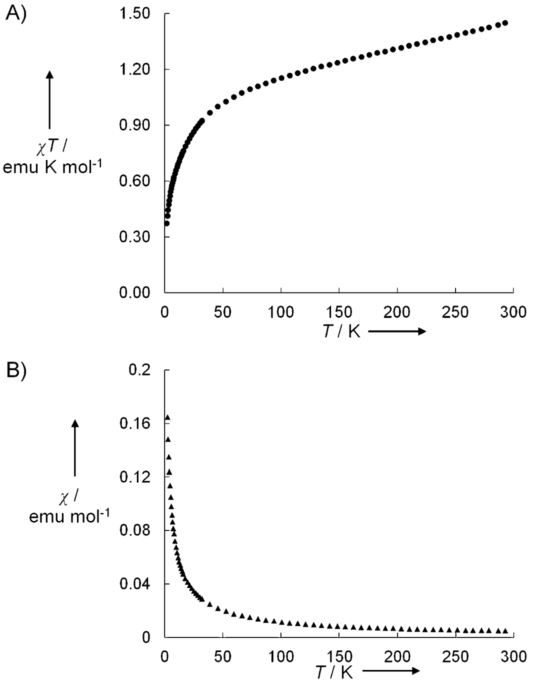

Figure 2. A) χT versus T and B) χ versus T plots of the temperature-dependent magnetic data collected at 1.0 T for $[K(Et_2O)]_2[U(NDIPP)_3]_2$ (**2**).

imido substituents in **2** eliminates π-bonding interactions, preventing that pathway for magnetic communication between the two U centers. This postulate is supported by the increase towards linearity of the U-N-C angle, which evidently disfavors communication between the two 5f^1 centers.

The studies presented here demonstrate the synthesis and reduction of a unique monomeric uranium tris(imido) species [U(NDIPP)$_3$(thf)$_3$] (**1**), which lacks traditional ancillary ligand frameworks, and its dimeric reduction product [K(Et$_2$O)]$_2$[U(NDIPP)$_3$]$_2$ (**2**). The coordinative unsaturation of **1** creates an interesting *cis* bonding motif, with no preference towards *trans*-imido bonding in the solid state as compared to previously synthesized uranyl and bis(imido) analogues. Future work on this system will be directed at understanding the *cis* arrangement of the imido substituents in both **1** and **2**, as well as their reactivity towards the activation of small molecules.

Keywords: imido · magnetic properties · multiple bonds · reduction · uranium

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