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Uranium–Nitrogen Multiple Bonding: The Case of a Four-Coordinate Uranium(VI) Nitridoborate Complex

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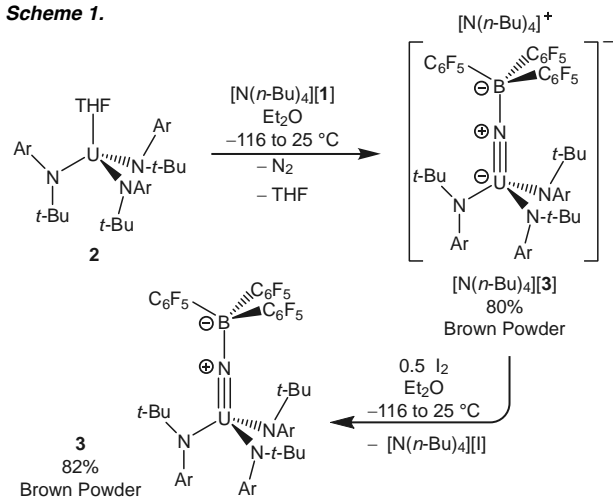
While uranium imido complexes are well established in the literature, complexes featuring a uranium nitride functionality are rare. Data pertaining to terminal uranium nitrides are limited to the spectroscopic observation of the binary uranium nitrides UN and NUN and the ternary nitride NUF₃ under matrix conditions.^{1–4} We are interested in the uranium nitride functional group as it incorporates metal–ligand multiple bonding, valence f orbitals, and redox activity.⁵

One typical route to metal nitride species involves the reaction of azide anion with reducing metal complexes.⁶ In uranium chemistry, this approach had led to bi- and polynuclear complexes with μ -nitrido ligands bridging two or more uranium centers.^{7–9} We posited that use of an azide salt complexed by a simple Lewis acid would deliver a protected nitride ligand to uranium without bimetallic complex formation. Accordingly, we now report the synthesis and characterization of the first nitridoborate complexes of uranium, complexes that alternatively may be viewed as borane-capped uranium nitrides (Scheme 1).

The structurally characterized azidoborate salt [NMe₄][(C₆F₅)₃B(N₃)] ([NMe₄][1])¹⁰ seemed to be an ideal candidate to test our approach for delivery of a protected nitride fragment to uranium. For convenience, we prepared the tetra-*n*-butylammonium derivative [N(*n*-Bu)₄][1] in good yield by treating [N(*n*-Bu)₄][N₃] with B(C₆F₅)₃ in CH₂Cl₂.¹¹ Dropwise addition of a thawing Et₂O solution of purple-black (THF)U(N[*t*-Bu]Ar)₃ (**2**, THF = tetrahydrofuran; Ar = 3,5-Me₂C₆H₃)¹² to a stirred thawing Et₂O solution of [N(*n*-Bu)₄][1] resulted in evolution of N₂ and a change in color to dark brown. A brown solid was isolated in 80% yield after allowing the reaction mixture to stir for 2 h and workup. The isolated material exhibited a solution μ_{eff} of 1.98 μ_{B} at 20 °C in CDCl₃, as determined by Evans's method,¹³ consistent with the formation of the uranium(V) complex [N(*n*-Bu)₄][(C₆F₅)₃B–N=U(N[*t*-Bu]Ar)₃] ([N(*n*-Bu)₄][3]). The solution μ_{eff} value for [N(*n*-Bu)₄][3] is lower than the theoretical value for a free 5f¹ ion (μ_{eff} = 2.54 μ_{B}), a feature typical in actinide systems.^{14,15}

Structural determination of [N(*n*-Bu)₄][3] by single crystal X-ray diffraction confirmed our formulation of the product, with [N(*n*-Bu)₄][3] crystallizing as discrete, spatially separated [N(*n*-Bu)₄]⁺ and [3][–] ions. The structure of [3][–] features a nearly linear B–N=U core (177.8(3)°). The B1–N4 distance of 1.540(6) Å is slightly longer than the corresponding distance in [NMe₄][1] (1.584(4) Å)¹⁰ and is short when compared to the range of B–N distances found in other reported pentafluorophenyl-substituted nitridoborate complexes (1.547–1.593 Å; avg. 1.580 Å).^{16–20} The U1–N4 distance of 1.916(4) Å is 0.1 Å shorter than the average U–N_{imido} distance calculated from several reported neutral uranium(V) imido complexes,^{15,21–24} but is essentially identical to the U–N_{imido} distance found in the related

Scheme 1.



tris(hexamethyldisilazide)uranium(V) complex Me₃Si–N=U(N[SiMe₃]₂)₃ (1.910(6) Å).²³

A solution of [N(*n*-Bu)₄][3] in THF was found by cyclic voltammetry to exhibit a reversible 1e[–] redox event at –0.60 V (vs. Fc/Fc⁺) assigned to the U⁵⁺/U⁶⁺ couple. Chemical oxidation of [N(*n*-Bu)₄][3] with I₂ (0.5 equiv) or AgOTf (1 equiv) in thawing Et₂O led to formation of the diamagnetic uranium(VI) complex (C₆F₅)₃B–N=U(N[*t*-Bu]Ar)₃ (**3**), which precipitated from solution upon concentrating the reaction mixture and adding *n*-pentane, and which was isolated in 82% yield.

The structure of **3**, as determined by single crystal X-ray diffraction, features a B–N=U core that is again nearly linear (179.4(3)°) and a B1–N4 distance of 1.592(6) Å, this being 0.05 Å longer than the corresponding distance in [3][–]. The U1–N4 distance of 1.880(4) Å is *ca.* 0.04 Å shorter than the corresponding distance in [3][–] and is shorter than the U=N distances in the five-coordinate uranium(VI) imido(fluoride) complexes *trans*-U(NR)(N[SiMe₃]₂)₃F (R = SiMe₃, Ph).²⁵ For comparison, the terminal uranium nitrides UN, NUN, and NUF₃ have U–N calculated distances of 1.746, 1.717 Å, and 1.759 Å, respectively.^{3,4} Lewis acid adducts of metal nitrides are known to display longer M–N distances than the corresponding free terminal nitrides.^{16,26}

To address the question of how the bonding in **3** compares to that of a free terminal uranium nitride or an organoimido uranium(VI) complex we turned to density functional theory and calculated U–N bond multiplicity (BM) indices based on Nalewajski-Mrozek valence indices.²⁷ This approach incorporates both covalent and ionic contributions to valency and yields BM indices, analogous to bond order, that correlate well with experimental observables such as interatomic distances and vibrational frequencies as well as chemically

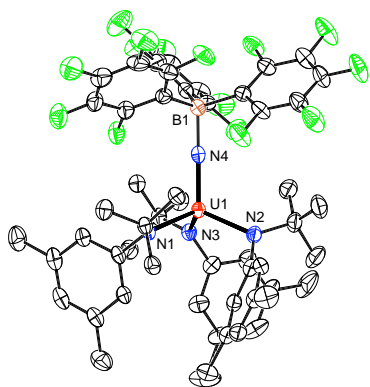


Figure 1. ORTEP rendering of **3**, ellipsoids displayed at 50% probability; hydrogen atoms and one molecule of co-crystallized Et₂O have been omitted for clarity. Selected bond lengths (Å) and angles (°): U1–N4, 1.880(4); N4–B1, 1.592(6); U1–N1, 2.193(3); U1–N2, 2.184(3); U1–N3, 2.194(4); B1–N4–U1, 179.4(3).

intuitive descriptions of bonding. This approach has recently been applied to metal–ligand and metal–metal multiply bonded systems with favorable results.²⁷

Table 1 collects the calculated U–N distances and BM indices for the truncated model (C₆F₅)₃B–N≡U(N[Me]Ph)₃ (**3m**) and several other relevant molecules (**4–10**).^{3,4,25,28–31} In all cases the calculated U–N distances agree well with the experimentally observed values and a linear relationship between BM and U–N distance is noted. Surprisingly, the calculated BM for the linear molecule **5** suggests a U–N quadruple bond, while the BM of the free terminal nitriles **6** and **7** are between that of a triple and quadruple bond.³² The calculated Mo–N BM for the related Mo complex **8m** falls below three. Notable as well are the large charges borne by both U and N (q_M and q_N) in **7**, reflecting greater polarization of the M–N bond as compared to **8m**. Upon moving from **7** to **3m** the U–N BM decreases to slightly less than that of a full triple bond, which is similar to the U–N BM values for the model organoimido complexes **9–11**; q_N for **3m** is similar as well to those of **9–11**. Thus, while **3** may be described as a borane adduct of a uranium nitride, from the standpoint of the U–N BM and q_N , **3** is an analogue of other formally triply bonded uranium(VI) organoimido complexes.

[N(*n*-Bu)₄][**3**] and **3** are the first examples of uranium nitridoborate complexes, and the synthesis of [N(*n*-Bu)₄][**3**] from [N(*n*-Bu)₄][**1**] demonstrates a new method for preparing nitridoborate complexes, one that does not require a free metal nitride as a precursor or the use of protic reagents.³³ Though precedent exists for the chemical removal of the borane fragment from nitridoborate complexes,¹⁶ **3** has not yielded to our attempts at deprotection.

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Supporting Information Available: Complete experimental details, characterization data, crystallographic and computational details, including crystallographic information files in CIF format and BM indices for several uranyl derivatives. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Table 1. A selection of calculated bond multiplicities.

Entry	Molecule ^a	Bond	Distance ^b	BM ^c	q_M^d	q_N^e
3m	(C ₆ F ₅) ₃ BNU(N[Me]Ph) ₃	U–NB	1.874 (1.880(4)) ^f	2.83	+3.18	–1.41
		U–NC ₂	2.193 (2.190) ^f	1.43		
		N–B	1.570 (1.592(5)) ^f	0.88		
4	(C ₆ F ₅) ₃ BNCMe	N–B	1.590 (1.616(3))	0.80		
5	NUN	U–N	1.743	4.07	+1.52	–0.76
6	NUF ₃	U–N	1.755	3.71	+2.16	–0.51
		U–F	2.066	1.56		
7	NU(N[Me]Ph) ₃	U–N	1.769	3.67	+3.44	–1.24
		U–NC ₂	2.216	1.36		
8m	NMo(N[Me]Ph) ₃	Mo–N	1.660 (1.651(4)) ^f	2.79	+1.69	–0.60
		Mo–NC ₂	1.990 (1.964) ^f	0.92		
9	U(N- <i>t</i> -Bu) ₂ (I) ₂ (THF) ₂	U–N	1.882 (1.844)	2.70	+2.82	–1.47
10	UCp* ₂ (NPh) ₂	U–N	1.984 (1.952(7))	2.36	+3.71	–1.34
11	U(NSiMe ₃)(N[SiMe ₃] ₂) ₃ F	U–N	1.943 (1.854(23))	2.62	+4.61	–1.52

^a All molecules geometry-optimized without symmetry constraints at the spin-restricted BP86 TZ2P/ZORA level.

^b Distances given in Å; average values are reported in cases with more than one of a given type; values listed in parentheses are experimentally observed distances.

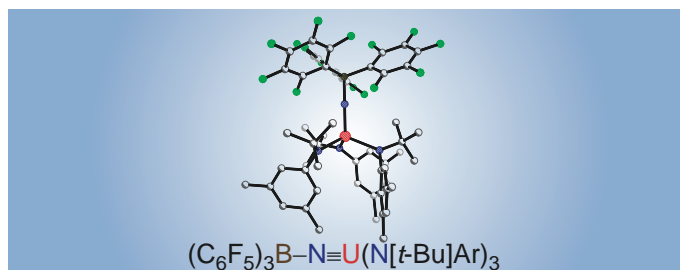
^c Bond multiplicity calculated as discussed and cited in the text.

^d MDC-q charge on the metal atom in atomic units.

^e MDC-q charge on the multiply-bonded N atom in atomic units.

^f Distance pertains to complex bearing the full –N[*t*-Bu]Ar ligand set.

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Reaction of the azidoborate salt $[\text{N}(n\text{-Bu})_4][(\text{C}_6\text{F}_5)_3\text{B}(\text{N}_3)]$ ($[\text{N}(n\text{-Bu})_4][\mathbf{1}]$) with the uranium(III) tris(anilide) complex $(\text{THF})\text{U}(\text{N}[t\text{-Bu}]\text{Ar})_3$ ($\mathbf{2}$; THF = tetrahydrofuran; Ar = 3,5-Me₂C₆H₃) results in formation of the paramagnetic uranium(V) nitridoborate complex $[\text{N}(n\text{-Bu})_4][(\text{C}_6\text{F}_5)_3\text{B}-\text{N}\equiv\text{U}(\text{N}[t\text{-Bu}]\text{Ar})_3]$ ($[\text{N}(n\text{-Bu})_4][\mathbf{3}]$). Chemical oxidation of $[\text{N}(n\text{-Bu})_4][\mathbf{3}]$ is facile and provides the diamagnetic uranium(VI) nitridoborate complex $(\text{C}_6\text{F}_5)_3\text{B}-\text{N}\equiv\text{U}(\text{N}[t\text{-Bu}]\text{Ar})_3$ ($\mathbf{3}$). $[\text{N}(n\text{-Bu})_4][\mathbf{3}]$ and $\mathbf{3}$ are the first nitridoborate complexes of uranium and were characterized by multinuclear NMR spectroscopy, single crystal X-ray diffraction methods, and elemental analysis. The X-ray crystal structures of $[\text{N}(n\text{-Bu})_4][\mathbf{3}]$ and $\mathbf{3}$ reveal extremely short U–N_{nitrido} distances (1.916(4) Å and 1.880(4) Å, respectively). Density functional theory was used to calculate the optimized structure of the truncated model $(\text{C}_6\text{F}_5)_3\text{B}-\text{N}\equiv\text{U}(\text{N}[\text{Me}]\text{Ph})_3$; the procedure was carried out similarly for several other relevant complexes featuring U–N multiple bonds. Bond multiplicities based on Nalewajski-Mrozek valence indices were calculated, the results of which suggest that the U–N_{nitrido} interaction in $\mathbf{3}$ is close to a full triple bond.
