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.\(^5,^6\)

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 polymetallic complexes with μ-nitrido ligands bridging two or more uranium centers.\(^7,^9\) We posited that use of an azide salt as 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 [N(Me4)][(C6F5)3B(N)] ([N(Me4)][I])\(^{10}\) seemed to be an ideal candidate to test our approach for delivery of a protected nitride fragment to uranium. For convenience, we prepared the candidate to test our approach for delivery of a protected nitridoborate complex [N(n-Bu)4][I]\(^{11}\) crystallizing as discrete, spatially separated equivalents, a μ-θ value for [N(n-Bu)4][I]\(^{12}\) to a stirred thioether solution of [N(n-Bu)4][I] resulted in evolution of N\(_2\) 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\(_{\text{eff}}\) of 1.98 μ\(_B\) at 20 °C in CDCl\(_3\), as determined by Evans’s method,\(^13\) consistent with the formation of the uranium(V) complex [N(n-Bu)4][[(C6F5)3B–N=n=N(n-Bu)[Ar]3]] ([N(n-Bu)4][3]). The solution μ\(_{\text{eff}}\) value for [N(n-Bu)4][I]\(^{13}\) is lower than the theoretical value for a free 5f\(^1\) ion (μ\(_{\text{eff}}\) = 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][I]\(^{14}\) 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)\(^{16}\) 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).\(^{17,18}\) The U1–N4 distance of 1.916(4) Å is 0.1 Å shorter than the average U–N\(_{\text{imid}}\) distance calculated from several reported neutral uranium(V) imido complexes,\(^19,21,24\) but is essentially identical to the U–N\(_{\text{imid}}\) distance found in the related tris(hexamethyldisilazide)uranium(V) complex Me\(_3\)Si–N=U[N(SiMe\(_3\))]\(_2\)F (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. Fe3+/Fe2\(^+\)) assigned to the U\(^{5+}/U\(^{6+}\) couple. Chemical oxidation of [N(n-Bu)4][3] with I\(_2\) (0.5 equiv) or AgOTf (1 equiv) in thawing Et\(_2\)O led to formation of the diamagnetic uranium(VI) complex (C\(_6\)F\(_5\))\(_3\)B–N=N(n-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 0.04 Å shorter 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(SiMe\(_3\))]\(_2\)F (R = SiMe\(_3\), Ph).\(^{25}\) For comparison, the terminal uranium nitrides UN, NUN, and NUF\(_3\) have U–N 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
intuitive descriptions of bonding. This approach has recently
been applied to metal-ligand and metal-metal multiply bonded
systems with favorable results.57

Table 1 collects the calculated U–N distances and BM
indices for the truncated model (C6F5)3B–N(Me)2Ph3
(3m) and several other relevant molecules (4-10),3,4,25-28,31 In
case of all 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
quadrapole bond, while the BM of the free terminal nitrides 6
and 7 are between that of a triple and quadrapole 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 (qN and qU) in 7, reflecting greater polarization
of the M–N bond as compared to 8m. Upon moving from 7 to
3 the U–N BM decreases to slightly less than that of a full
tripe bond, which is similar to the U–N BM values for the
model organoimido complexes 9-11; qN for 3m is similar as
good as 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 qN, 3 is an analogue of other formally tripoly
bonded uranium(VI) organoimido complexes.

[N(n-Bu)3]3 and 3 are the first examples of uranium nitridoare complexes, and the synthesis of [N(n-Bu)3]3
from [N(n-Bu)3]1 demonstrates a new method for preparing
nitridoare 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 nitridoare complexes,6 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.

References

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* All molecular geometries-optimized without symmetry constraints at the spin-restricted BP86/TZP/321G level.

** Distance given in Å, averages are reported in cases where more than 1 disagreement when listed

*** Bond multiplicity calculated as described and cited in the text.

### References

Reaction of the azidoborate salt \([N(n-Bu)_4]([C_6F_5)_3B(N_3)]\) with the uranium(III) tris(anilide) complex (THF)U(N[t-Bu]Ar)_3 (2; THF = tetrahydrofuran; Ar = 3,5-Me_2C_6H_3) results in formation of the paramagnetic uranium(V) nitridoborate complex \([N(n-Bu)_4][(C_6F_5)_3B–N\U(N[t-Bu]Ar)_3]\) (3). Chemical oxidation of \([N(n-Bu)_4][1]\) is facile and provides the diamagnetic uranium(VI) nitridoborate complex \((C_6F_5)_3B–N\U(N[t-Bu]Ar)_3\) (3). \([N(n-Bu)_4][1]\) and 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 \([N(n-Bu)_4][3]\) and 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 \((C_6F_5)_3B–N\U(N[Me]Ph)_3\); 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 3 is close to a full triple bond.