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Uranium–Nitrogen Multiple Bonding: Isostructural Anionic, Neutral, and Cationic Uranium Nitride Complexes Featuring a Linear U=N=U Core

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Supporting information:
Experimental details, including treatment of [3][B(ArF)4] with CO and LiCCPh; crystallographic data and files in CIF format; and computational data relevant to the electronic structure of 3. This material is available free of charge via the Internet at http://pubs.acs.org

Graphical abstract:
Abstract

Reaction of the uranium(III) tris(anilide) complex (THF)U(N[n-Bu]Ar)₃ (1, THF = tetrahydrofuran; Ar = 3,5-Me₂C₆H₃) with [N(n-Bu)]₃[B(N₃)(C₆F₅)]₃, which directly furnishes the monometallic uranium(V) nitridoborate complex [N(n-Bu)]₃[B(N₃)(C₆F₅)] (2) and provides access to the neutral uranium(VI) nitridoborate derivative (C₆F₅)₃B−N=U[N(n-Bu)Ar] (3) by one-electron oxidation of [N(n-Bu)]₃[B(N₃)(C₆F₅)] (2). In the synthesis of [N(n-Bu)]₃[B(N₃)(C₆F₅)] (2), the tris(pentafluorophenyl)boron fragment serves the role of protecting group by preventing the formation of polymetallic μ-nitrido products, thus facilitating isolation of the first examples of molecular monometallic uranium nitrides. Herein, we report on complexes derived from the action of unprotected azide ion on 1, a series of bimetallic uranium nitride complexes possessing a linear U≡N≡U core that is stable across several charge states.

Introduction

Uranium nitrides have been identified as worthy candidates for N-atom transfer reactions and aziridination of small molecules, and their potential use in catalytic cycles and as advanced nuclear fuels has been noted. To date, only a handful of uranium nitride complexes have been reported, most of which are polymetallic nitride clusters derived from dinitrogen or azide activation and binary and ternary nitrides generated and observed under matrix-isolation conditions. Beyond uranium nitrides, assessing the degree of covalency and mixing of 5f and 6d orbitals in actinide−ligand bonding continues to be an active area of research and has been recently extended to multiply bonded uranium imido complexes shown to accommodate multiple formal oxidation states at uranium.

We recently reported on the reaction of (THF)U(N[n-Bu]Ar)₃ (1, THF = tetrahydrofuran; Ar = 3,5-Me₂C₆H₃) with [N(n-Bu)]₃[B(N₃)(C₆F₅)]₃, which directly furnishes the monometallic uranium(V) nitridoborate complex [N(n-Bu)]₃[B(N₃)(C₆F₅)] (2) and provides access to the neutral uranium(VI) nitridoborate derivative (C₆F₅)₃B−N=U[N(n-Bu)Ar] (3) by one-electron oxidation of [N(n-Bu)]₃[B(N₃)(C₆F₅)] (2). In the synthesis of [N(n-Bu)]₃[B(N₃)(C₆F₅)] (2), the tris(pentafluorophenyl)boron fragment serves the role of protecting group by preventing the formation of polymetallic μ-nitrido products, thus facilitating isolation of the first examples of molecular monometallic uranium nitrides. Herein, we report on complexes derived from the action of unprotected azide ion on 1, a series of bimetallic uranium nitride complexes possessing a linear U≡N≡U core that is stable across several charge states.
Treatment of a purple-black solution of 1 in THF with NaN₃ (0.5 equiv) resulted in a gradual color change to red-brown over ~12 h. A rust-brown powder was isolated in 70% yield following workup. The paramagnetically broadened ¹H NMR spectrum, solution magnetic susceptibility (μₑff = 3.23 μB, 20 °C, THF-d₈), and combustion analysis of the isolated material were consistent with the formation of the bimetallic diuranium(IV/IV) complex Na[(μ-N)(U(N[t-Bu]Ar)₃)_2] (Na[3]). Similarly, treatment of 1 with [N(n-Bu)₄][N₃] (0.5 equiv) in thawing THF provided [N(n-Bu)₄][3] (μₑff = 3.22 μB, 20 °C, THF-d₈) in 79% yield.

With a formal 5f² electron count for each uranium(IV) center in the bimetallic [3]⁻ ion, the possibility for rich redox chemistry was realized (Scheme 1). Indeed, addition of AgOTf (1 equiv) to a solution of Na[3] in THF resulted in formation of the neutral diuranium(IV/V) complex [(μ-N)(U(N[t-Bu]Ar)₃)_2](3; μₑff = 3.85 μB, 20 °C, chloroform-d₈), which was isolated as a brown powder in 70% yield by precipitating and filtering off the product following removal of precipitated Ag₀ and separation from NaOTf. Furthermore, 3 reacted with [Cp₂Fe][B(ArF)₄] [ArF = 3,5-(CF₃)₂C₆H₃] in Et₂O to form the cationic diuranium(V/V) complex [(μ-N)(U(N[t-Bu]Ar)₃)_2][B(ArF)₄] ([3][B(ArF)₄]; μₑff = 2.86 μB, 20 °C, chloroform-d₈), which was separated from the ferrocene coproduct by precipitation and isolated in 93% yield by filtration. The electrochemical potentials relating [3]⁻, 3, and [3]⁺ were measured via cyclic voltammetry using a solution of 3 in THF. Two reversible electrochemical events at E₁/₂ = −1.69 and −0.64 V (vs [Cp₂Fe]⁰⁰⁺) were observed and assigned to the [3]⁻/3 and 3/[3]⁺ couples, respectively (Figure 1). The large separation between the [3]⁻/3 and 3/[3]⁺ couples (∆E₁/₂ = 1.05 V) corresponds to an equilibrium constant Kₑ ≈ 5.6 × 10¹⁷ for the comproportionation of [3]⁻ and [3]⁺, suggesting strong electronic communication between the uranium centers.³ A third electrochemical event observed at potentials above 0 V was not fully reversible at sweep rates as fast as 1000 mV s⁻¹ and may be due to formation of an unstable [3]²⁺ species.

![Figure 1. Cyclic voltammogram of 3 in THF (200 mV s⁻¹ sweep rate, ~0.1 M [N(n-Bu)₄][B(C₆F₅)₄] supporting electrolyte) showing the two one-electron redox couples that interconvert [3]ⁿ (n = −1, 0, +1).](image-url)
Scheme 1.

The solid-state structures of [N(n-Bu)$_4$][3], 3 (Figure 2), and [3][B(Ar$^r$)$_4$]$_3$ were determined by single-crystal X-ray diffraction, providing a rare opportunity to compare structural parameters of a U–N multiple bond over three charge states. Key metrical parameters describing the structures of [3]$^n$ ($n = -1, 0, +1$) are summarized in Table 1. In all cases, each uranium center is coordinated in a trigonal pseudo-C$_3$ fashion by three anilide ligands and occupies a terminus of a linear U═N═U bridge. Successive one-electron oxidation of the U═N═U core results in a decrease of the U–N$_{nitride}$ distance across a range of ~0.03 Å, while the average U–N[n-Bu]Ar distance decreases across a comparably larger range of ~0.12 Å. The observed contraction of the U═N═U core upon oxidation is likely primarily electrostatic in origin, where the removal of metal-based nonbonding electrons results in an increasingly electron-deficient U═N═U core. This structural dependence on charge is reminiscent of that displayed by penta- and hexavalent uranyl complexes, where the very covalent multiple bonds along the O═U═O axis are less responsive to the charge state than are the more ionic bonds in the molecular equator. The U–N$_{nitride}$ distances of the [3]$^n$ series fall in a range that is ~0.1 Å longer than typical U–N distances observed in uranium imido complexes and are similar to those found in the octanuclear mixed
azide/nitride clusters $[{(C_5Me_4R)}_2U(\mu-N)(C_5Me_4R)U(\mu-N_3)]_4$ (R = H, Me) reported by Evans and co-workers \cite{2c} (see Table S.2 in the Supporting Information for a more detailed comparison of relevant bond metrics).

![ORTEP rendering of 3](image)

**Figure 2.** ORTEP rendering of 3 with ellipsoids displayed at 50% probability; hydrogen atoms and one molecule of cocrystallized Et₂O have been omitted for clarity.

<table>
<thead>
<tr>
<th>$[N(n$-Bu$)_4]_3$</th>
<th>3</th>
<th>$[3][B(Ar^F)_4]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>U–N</td>
<td>2.080(4)</td>
<td>2.0625(2)</td>
</tr>
<tr>
<td>U–N$[r$-Bu$]Ar$ (avg)</td>
<td>2.077(4)</td>
<td>2.0511(3)</td>
</tr>
<tr>
<td>U–N–U</td>
<td>175.1(2)</td>
<td>180</td>
</tr>
</tbody>
</table>

Table 1. Internuclear Distances (Å) and Angles (deg) for $[(\mu-N)(U(N[t$-Bu$]Ar)_3)_2]^n$ ($n = -1, 0, +1$)

Treatment of $[3][B(Ar^F)_4]$ in THF with NaCN results in elimination of Na[B(Ar$^F$)$_4$] and formation of the known diuranium(IV/IV) cyanoimide complex $(\mu-NCN)(U(N[t$-Bu$]Ar)_3)_2$ (4), which by this new reaction was isolated in 60% yield (Scheme 2). Prior to its synthesis from NaCN and $[3][B(Ar^F)_4]$, 4 had been prepared from 1 and a cyanonitrene ($N\equiv C$–N) group transfer reagent. \cite{9} Here, cyanide serves as a two-electron reducing agent, converting two uranium(V) centers to uranium(IV) while inserting into the nitride bridge. This is similar to a reaction reported by Meyer and co-workers \cite{10} wherein a monometallic uranium(V) imido complex $[(L)U(NSiMe_3)]$ reacts with methyl isocyanide to form Si$_2$Me$_6$ and the uranium(IV) carbodiimide derivative $[(L)U(NCNMe)]$. More generally, Scheme 2 relates to the known reactivity of certain electrophilic metal nitride complexes toward reducing Lewis bases such as phosphines or carbon monoxide, yielding
phosphiniminato or isocyanate derivatives, respectively,\(^{11}\) and shows as well that the U═N═U core of [3]\(^+\) behaves as a masked metallonitrene.\(^ {12}\)

**Scheme 2.**

The complexes reported here provide insight into the structural and electrochemical characteristics of uranium nitrides. Insertion of cyanide into the U═N═U core of [3][B(Ar\(^5\))\(_4\)] shows that the reaction chemistry of uranium nitrides extends beyond simple outer-sphere redox processes. This, along with the high polarity expected of a terminal uranium–nitride bond (U\(^{δ+}\)−N\(^{δ−}\)) and the oxidizing nature of uranium in its higher oxidation states, intimates that a high-valent terminal uranium nitride would have the capacity to engage in bond-forming reactions at the nitride ligand via multiple mechanistic pathways. Further developments stemming from this system of uranium nitrides may be anticipated, especially regarding reactions that result in heterolytic fragmentation of the U═N═U core.
References


