

Synthesis and Structure of Nitride-Bridged Uranium(III) Complexes

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S Supporting Information

ABSTRACT: The reduction of the nitride-bridged diuranium(IV) complex $\text{Cs}_2[\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_2(\mu\text{-N})\}]$ affords the first example of a uranium nitride complex containing uranium in the +III oxidation state. Two nitride-bridged complexes containing the heterometallic fragments $\text{Cs}_2[\text{U}^{\text{III}}\text{---N---U}^{\text{IV}}]$ and $\text{Cs}_3[\text{U}^{\text{III}}\text{---N---U}^{\text{III}}]$ have been crystallographically characterized. The presence of two or three Cs^+ cations binding the nitride group is key for the isolation of these complexes. In spite of the fact that the nitride group is multiply bound to two uranium and two or three Cs^+ cations, these complexes transfer the nitride group to CS_2 to afford SCN^- and uranium(IV) disulfide.

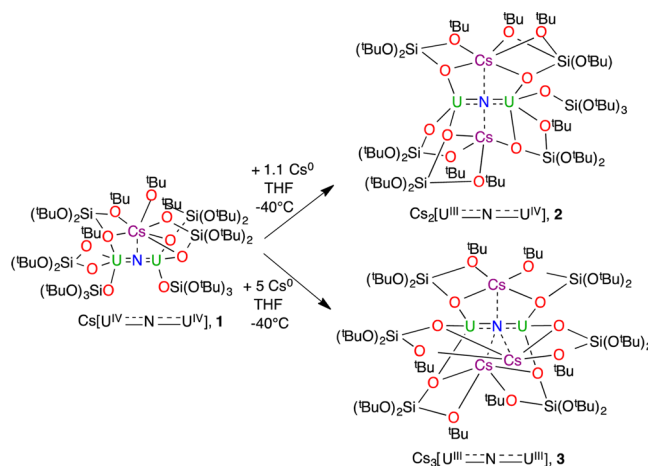
Molecular uranium nitrides are attractive synthetic targets because of their potential as precursors to ceramic materials or as efficient molecular catalysts.¹ Notably, uranium(III) mononitride, UN ,² a solid that is difficult to synthesize and solubilize, has been proposed for alternative nuclear fuels³ and as an effective catalyst in dinitrogen reduction to ammonia.⁴ Moreover, molecular nitride complexes are also important to gain a better understanding of *f* orbital implication in multiple bonding and covalency in actinide–ligand bonds.⁵ Uranium nitride chemistry remains much less developed than the *d*-block counterparts. In recent years several molecular complexes of uranium have been prepared that contain nitride groups bridging two or more uranium ions⁶ or terminal nitride groups.⁷ Most of these complexes contain uranium in its +IV oxidation state, with a few systems containing U(V) and U(VI). In spite of their relevance in materials science and catalysis and the anticipated attractive reactivity of uranium(III) nitrides, no molecular uranium(III) nitride complex has been isolated in solution or in the solid state. The isolation of molecular uranium(III) nitrides is essential for investigating the reactivity of the $\text{U}^{\text{III}}\text{---nitride}$ bond, which in turn will lead to convenient routes to nitride materials and the design of molecular catalysts. Here we report the first examples of nitride-bridged complexes containing uranium in the +III oxidation state.

Recently we reported the synthesis and molecular structure of the dinuclear uranium(IV)/uranium(IV) nitride $\text{Cs}_2[\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_2(\mu\text{-N})\}]$ (**1**). This complex remains a rare example^{6f,h} of a dinuclear uranium nitride complex featuring a linear $\text{U}^{\text{IV}}\text{---N---U}^{\text{IV}}$ fragment (U---N---U angle = $170.2(3)^\circ$) and short U---N distances (U1---N1 , 2.058(5) Å; U2---N1 , 2.079(5) Å) indicative of U---N multiple bonds. Moreover, in complex **1** the Cs^+ cation binds the bridging nitride and six oxygen atoms from the siloxide ligands, affording a unique

heterometallic structure. The ability of the $\text{OSi}(\text{O}^t\text{Bu})_3$ ligand to bind to Cs^+ , thus stabilizing highly charged species, motivated us to explore the possibility of stabilizing the $\text{U}^{\text{III}}\text{---N---U}$ fragment in highly reduced uranium species.

The reduction of complex **1** with 1 equiv or a large excess of Cs^0 in tetrahydrofuran (THF) at -40°C under argon allowed the synthesis and characterization of the U(III)/U(IV) complex $\text{Cs}_2[\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_2(\mu\text{-N})\}]$ (**2**) in 67% yield and the U(III)/U(III) complex $\text{Cs}_3[\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_2(\mu\text{-N})\}]$ (**3**) in 77% yield, respectively (Scheme 1). The solid-state molecular

Scheme 1. Synthesis of $\text{Cs}_2[\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_2(\mu\text{-N})\}]$ (**2**) and $\text{Cs}_3[\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_2(\mu\text{-N})\}]$ (**3**)



structures of complexes **2** and **3** were determined by single-crystal X-ray diffraction (Figures 1 and 2). In both complexes **2** and **3**, each uranium ion is coordinated by a nitride group and three siloxide oxygens with a pseudotetrahedral geometry. The two U---N distances in complex **3** are equivalent as a result of the twofold crystallographic axis passing through one Cs and the nitride ion. In complex **2** the two U---N distances are similar (Table 1), suggesting the presence of nonlocalized charge.

In all of the complexes **1–3**, the Cs^+ cations are bound to the bridging nitride and to the siloxide oxygens. In complex **2**, two Cs^+ cations bind the nitride in an almost linear way (Cs---N---Cs angle = $161.8(4)^\circ$) with the Cs---N---Cs and the $\text{U}^{\text{III}}\text{---N---U}$ fragments located in the same plane and perpendicular to each other. In complex **3**, the three Cs^+ cations bind the nitride to form an irregular triangle located in a plane perpendicular to the $\text{U}^{\text{III}}\text{---N---U}$ fragment (Cs---N---Cs angles: $119.1(4)$,

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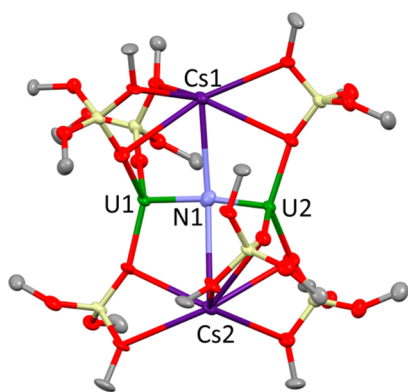


Figure 1. Crystallographic structure of $\text{Cs}_2[\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_2(\mu\text{-N})\}]$ (2) crystallized from a saturated THF solution. The ellipsoid probability is 50%, and hydrogen atoms, methyl groups, and solvent molecules have been omitted for clarity. Atoms: C (gray), O (red), Si (light yellow), N (light blue), Cs (purple), and U (green).

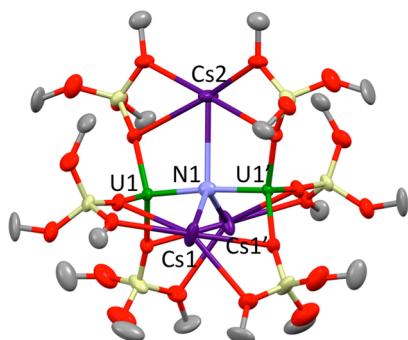


Figure 2. Crystallographic structure of $\text{Cs}_3[\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3(\mu\text{-N})\}]$ (3) crystallized from a saturated THF solution. The ellipsoid probability is 50%, and hydrogen atoms, methyl groups, and disorder on Cs2 have been omitted for clarity. Atoms: C (gray), O (red), Si (light yellow), N (light blue), Cs (purple), and U (green).

108.9(3), and 132.0(7)°. The Cs–N distances are longer than those found in an imido-bridged U(IV) complex (mean Cs–N = 3.075(10) Å).^{7d}

Complexes 2 and 3 display a linear $\text{U}^{\text{III}}\text{---N}^{\text{III}}\text{---U}^{\text{IV}}$ motif with U–N–U angles comparable to that found in complex 1 (Table 1). The U–N distances in complexes 2 and 3 fall in the range 2.081–2.1495 Å and are longer than those found in **1**^{6g} and previously reported U(IV)/U(V) nitrides containing the linear $\text{U}=\text{N}=\text{U}$ motif (2.012(16)–2.090(8) Å).^{6a,f,h} These distances remain much shorter than U(III)–N single-bond distances (e.g., $\text{U}-\text{N}_{\text{cyanate}} = 2.456(7)$ Å,⁸ $\text{U}-\text{N}_{\text{dinitrogen}} = 2.401(8)$ – $2.423(8)$ Å,⁹ and $\text{U}-\text{N}_{\text{amide}} = 2.320(4)$ Å in $\text{U}[\text{N}(\text{SiMe}_3)_2]_3$ ¹⁰). Longer U–N distances were also found in a U(IV) cluster with a $\text{U}_4(\mu_4\text{-N})$ core (2.271(3)–2.399(5) Å).^{6d} This points to the presence of $\text{U}^{\text{III}}\text{---N}$ multiple bonding in 2 and 3. The mean

value of the U–N bond distance in the nitride core increases by about 0.08 Å in the fully reduced $\text{Cs}_3[\text{U}^{\text{III}}\text{---N}^{\text{III}}\text{---U}^{\text{III}}]$ system compared with the $\text{Cs}[\text{U}^{\text{IV}}\text{---N}^{\text{III}}\text{---U}^{\text{IV}}]$ unit, probably as a result of the presence of additional electrons at the uranium center. Such an increase is similar to the increase in the average U–O bond length (0.09 Å), which can be related to the difference between the ionic radii of U(III) and U(IV) (0.135 Å). A smaller variation (0.03 Å) was observed by Cummins and co-workers in the successive oxidation of a linear $\text{U}(\text{IV})=\text{N}=\text{U}(\text{IV})$ fragment supported by amide ligands to $\text{U}(\text{V})=\text{N}=\text{U}(\text{V})$.^{6f} The larger variation observed in the successive reduction of the siloxide complex 1 is at least partly due to the presence of an increasing number of Cs^+ cations binding the nitride group and thus polarizing and reducing the electron density on the $\text{U}^{\text{III}}\text{---N}^{\text{III}}\text{---U}^{\text{IV}}$ fragment. Lengthening of U–N bonds upon alkali-metal ion coordination to the N atom has been observed in dinuclear U(IV) imido complexes.^{7d}

Complex 2 can be prepared analytically pure and stored in the solid state under argon at -40 °C for several weeks, but it is very reactive and can only be handled in solution at -40 °C. Complex 3 can be obtained analytically pure but decomposes very quickly both in the solid state and in THF solution at -40 °C, yielding mixtures of complexes 2 and 3 and free siloxide ligand. The extremely high reactivities of complexes 2 and 3 are in agreement with the absence in the literature of any molecular nitride compounds containing uranium in the +III oxidation state. The presence of the multidentate siloxide groups capable of binding the Cs^+ cation is key to the isolation of complex 3. Notably, the reduction of 1 with an excess of Cs^0 in the presence of crown ether 18C6 leads to intractable reaction mixtures containing the free ligand as the only NMR-detectable species. This indicates that when the Cs^+ cation is removed by the crown ether from the coordination pocket formed by the siloxide ligands in 1, it becomes impossible to isolate the $[\text{U}^{\text{III}}\text{---N}^{\text{III}}\text{---U}^{\text{III}}]^{3-}$ species from the reduction of 1. The proton NMR spectra of complexes 2 and 3 in THF solution show the presence of only one signal for the six siloxide ligands, in agreement with the presence of symmetry-related siloxides. In the case of complex 2, this can be interpreted in terms of the fluxionality of the bound Cs cation. Proton NMR studies showed that the addition of crown ether to complex 2 in THF results in the removal of the bound Cs^+ , leading to a significant decrease in the stability. In contrast, the addition of crown ether to complex 3 in THF does not lead to Cs removal.

Significant changes were also observed in the cyclic voltammogram of 1 when the electrochemistry was carried in the presence of 18C6. The cyclic voltammogram of complex 1 measured in THF (see the Supporting Information) shows two irreversible electrochemical events at -2.34 and -0.92 V (vs $[\text{Cp}_2\text{Fe}]^{0/+}$), corresponding to reduction and oxidation of the complex. The irreversibility of these redox events is probably

Table 1. Comparative Structural Parameters of Complexes 1–3

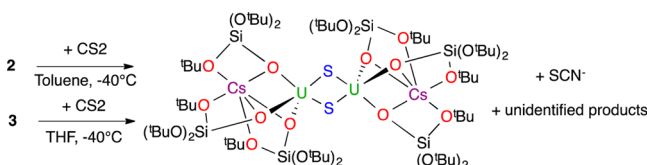
	$[\text{U}^{\text{IV}}\text{---N}^{\text{III}}\text{---U}^{\text{IV}}]$ (1)	$[\text{U}^{\text{III}}\text{---N}^{\text{III}}\text{---U}^{\text{IV}}]$ (2)	$[\text{U}^{\text{III}}\text{---N}^{\text{III}}\text{---U}^{\text{III}}]$ (3)
U1–N (Å)	2.058(5)	2.099(12)	2.1495(12)
U2–N (Å)	2.079(5)	2.081(12)	
U–O _{avg} (Å)	2.19(3)	2.243(25)	2.282(24)
Cs1–N (Å)	3.393(4)	3.276(12)	3.348(8)
Cs2–N (Å)	–	3.635(12)	3.22(2)
U–N–U (deg)	170.2(3)	169.1(7)	174.2(11)

due to the important rearrangement of the coordination sphere during the redox processes. After removal of Cs^+ , the reduction wave is shifted to lower potential ($E_{\text{pc}} = -2.43$ V), indicating that the reduction of complex **1** is more difficult in the absence of coordinated Cs^+ .

Complexes **2** and **3** provide the first examples of isolated molecular nitride complexes containing uranium in the +III oxidation state. These systems are expected to show high reactivity with a wide range of substrates because of the low oxidation state of uranium.¹¹ Previous reactivity studies of nitride-bridged uranium compounds are limited to a single example in which the $\text{U}^{\text{IV}}=\text{N}=\text{U}^{\text{IV}}$ fragment reacts as a masked metallonitrene with NaCN .^{6f}

Preliminary reactivity studies carried out with CS_2 showed that complexes **2** and **3** can transfer the nitride group to electrophilic substrates in spite of the fact that the nitride group is located in a protective pocket provided by the siloxide ligands and the multimetallic binding by two U and three Cs cations (see figures in the Supporting Information). The reactivity of complexes **2** and **3** with CS_2 is in agreement with a nucleophilic character of the nitride. Notably, the addition of $^{13}\text{CS}_2$ at -40 °C in THF to the bridging nitride led to the isolation of the disulfide-bridged diuranium(IV) complex ($\text{Cs}(\text{THF})_2[\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3\}_2(\mu\text{-S})_2]$ (**4**) in 25% yield (Scheme 2), which

Scheme 2. Reactivities of $\text{Cs}_2[\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3\}_2(\mu\text{-N})]$ (2**) and $\text{Cs}_3[\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3\}_2(\mu\text{-N})]$ (**3**) with CS_2**



was characterized by X-ray diffraction (see the Supporting Information). ^{13}C NMR monitoring of the reaction mixture allowed the product of nitride transfer to CS_2 to be identified as thiocyanate (SCN^-). The disulfide complex is thus likely to be formed by extrusion of CsSCN from a highly reactive dithiocarbamate intermediate. Proton NMR studies showed that the formation of **4** occurs immediately even at low temperature, and it was not possible to isolate any intermediate. Similar reactivity has been reported for a terminal V(V) nitride, but in that case the decomposition was slower and the dithiocarbamate intermediate was isolated.¹² However, the formation of **4** involves oxidation of the metal center from U(III) to U(IV), and therefore, additional products must be formed that remain unidentified.

In conclusion, here we have expanded the family of molecular uranium nitride complexes to include the +III oxidation state. This has been accomplished by reducing the U(IV) analogue with cesium metal. Structural studies point to the presence of $\text{U}^{\text{III}}-\text{N}$ multiple bonding. Future studies will be directed to further investigation of the nature of the U–N bonding in these systems. The reported reactivity with CS_2 is in agreement with a nucleophilic character of the nitride group. These complexes associating the highly reducing uranium(III) ion to a multiply bonded nitride group provide unprecedented precursors for the discovery of novel reactivity and unusual transformations. We are currently investigating the reactivities of these complexes with various substrates.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b12620.

Experimental procedures and spectral data (PDF)

Crystallographic data for **4** (CIF)

Crystallographic data for **3** (CIF)

Crystallographic data for 2·2THF (CIF)

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Notes

The authors declare no competing financial interest.

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