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Heterometallic uranium/molybdenum nitride synthesis via partial N-atom transfer

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Abstract: The reaction of a terminal Mo(II) nitride with a U(III) complex yields an heterodimetallic U-Mo nitride which is the first example of a transition metal-capped uranium nitride. The nitride is triply bonded to U(V) and singly bonded to Mo(0) and supports a U-Mo interaction. This compound shows reactivity toward CO oxidation.

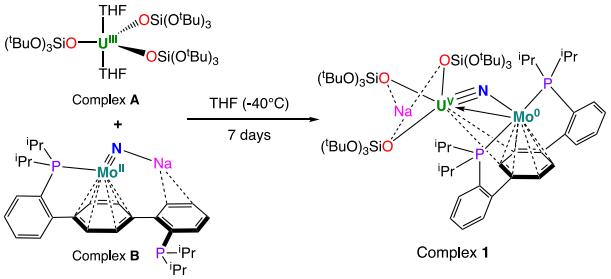
Metal nitrides are intermediates in the biological and industrial conversion of dinitrogen to ammonia and in N-transfer processes.[1a , 1b-g] Ternary nitrides generate catalysts with higher activity than the iron catalyst currently used in the Haber–Bosch process highlighting the potential of mixed metal nitrides.[2] Molecular uranium nitrides are attracting an increasing number of studies because of their high reactivity with small molecules such as CO_2, H_2, CO and N_2.[3] Notably, we recently showed that multimetallic uranium-alkali ion nitride complexes effect the reduction and subsequent functionalization of dinitrogen.[3f] However, despite important recent progress in the field, synthetic routes to uranium nitrides remain scarce and heterometallic nitrides are so far limited to asymmetric U≡N-M with M being an alkali ion, where the interaction of the nitride with the alkali ion is primarily ionic.[4a, 3c, 4b, 4c] In contrast, heterometallic UNM complexes with a N-M covalent bond are so far limited to a single U=N=Th example reported by Hayton and coworkers in 2021,[5] despite their potential applications in understanding dinitrogen activation and development of Haber-Bosch catalysts.[6]

Uranium nitrides have so far been generated only by N_2 cleavage, by reduction or photolysis of azide precursors or by chemical manipulation of uranium nitride and imide precursors.[7a-7i, 4a-4c, 3c, 3h, 3k]

Here we show that uranium nitrides can also be synthesised via a partial N-transfer redox reaction[8] from a low-oxidation state molybdenum nitride to a uranium(III) complex providing a convenient route to heterometallic U-transition metal (TM) nitrides.

We report the synthesis of the first example of a heterometallic uranium nitride complex where the nitride bridges uranium and a d-block ion. The complex [Na{(U(OSi(O^{t}Bu)$_3$(μ-N)(MoP2)}], **1** was prepared by partial N-transfer to the U(III) tris-siloxide complex [U(OSi(O^{t}Bu)$_3$)$_3$(thf)$_2$], **A**[9] from the Na-capped Mo(II) nitride **B** (Scheme 1). The nature of the U-N-TM bond in **1** is elucidated by structural, EPR and computational studies.

Preliminary ^{1}H NMR studies showed that the Mo(IV) nitride [Cl(N)MoP2] (P2= terphenyl diphosphine ligand)[10] does not react with 1-2 equiv [U(OSi(O^{t}Bu)$_3$)$_3$(thf)$_2$], **A.**[9]



Scheme 1. Synthesis of [Na{(U(OSi(O^{t}Bu)$_3$(μ-N)(MoP2)}], **1.**

This is consistent with the low nucleophilic character of the nitride in the Mo(IV) complex. In contrast, ^{1}H NMR studies showed that the reaction of [U(OSi(O^{t}Bu)$_3$)$_3$(thf)$_2$], **A**[9] with 1 equiv. of the Mo(II) terminal nitride [Na(N)MoP2], **B** at -40°C in thf led to the full consumption of the reagents over the course of 3 hours and the formation of a new species together with the previously reported [U(OSi(O^{t}Bu)$_3$)$_4$],[7c] probably resulting from side redox and ligand redistribution reactions. Cooling down the concentrated hexane solution of the reaction mixture afforded dark brown crystals of the heteronuclear bridging nitride complex [Na{(U(OSi(O^{t}Bu)$_3$}(μ-N)(MoP2)}], **1** in 72% yield.

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Performing the reaction at 25°C led to the full consumption of the starting materials over the course of 1 hour but only resulted in the formation of complex $[U(OSi(O^tBu)_3)_4]$ and other unidentified species. **1** can be stored at -40°C in the solid state at least up to a month, but decomposes rapidly in THF solution yielding a mixture of species from which only complex $[U(OSi(O^tBu)_3)_4]$ could be identified.

The solid-state molecular structure of **1** (Figure 1) shows a U-Mo heterometallic complex, with a nitride group bridging the U and the Mo centres in close proximity with a short U-Mo distance of 3.1032(2) Å, which compares well with the sum of the covalent radii of U and Mo (3.08)[11]. This value is slightly shorter than that found in the heterometallic U-Mo complexes displaying a U-Mo interaction, where the U and Mo centres are bridged by three phosphinoamide ligands (3.1682(4), 3.159(2) Å).[12] The short contact highlights the ability of the bridging ligands in **1**, a bent nitride and a phosphino arene to facilitate metal-metal interaction.[13] Relative to precursor **B**, the Na^+ cation is displaced from the Mo nitride moiety by the U ion and in **1** is found in the coordination site formed by the siloxide ligands. The U centre is heptacoordinated in a distorted capped trigonal prismatic geometry by three oxygen atoms from the siloxide ligands, the bridging nitride, the η^2-bound arene ring of the P2 ligand and the metal-metal contact.

The U-N distance (1.856(2) Å) is very short and indicative of a multiple U≡N bond interaction. The U-N distance is shorter than in previously reported diuranium(V) nitride complexes (U-N distances in the range 2.022(5) Å-2.101(6)Å),[7c, 3f, 3h] indicating that the nitride in **1** is asymmetrically shared between the metals, with U having a stronger interaction. While slightly longer than those found in U(VI) nitrides complexes (1.769 (2) and 1.799(7) Å),[14, 7g] the U-N distance in complex **1** is comparable to the two previously reported Na^+-capped U(V) terminal nitride complexes (1.883(4) Å and 1.835(5) Å).[4a, 4c]

Consistently, the Mo-N distance (2.148(2) Å) is considerably elongated compared to the Mo≡N distance found in the K-capped Mo(II) nitride analogue of **B** (1.728(3) Å)[17] or in Mo(IV) nitrides (1.642(2) Å) supported by the P2 ligand[17] and is similar to the Mo-N_{azide} (2.140(2) Å) distance in the Mo(IV) complex $[(N)(N_3)MoP2]$[17] the Mo-$N_{acetonitrile}$ (av 2.13 Å) in Mo(II) complex $[(MeCN)_2MoP2)^{2+}]$, and the Mo-N (2.037(2) Å) in Mo(0) complex $[(N_2)MoP2]$,[16] suggesting a Mo-N single bond. The UNMo moiety is bent (U1-N1-Mo1 angle: 101.1(1)°) and close to a right angle.

The central arene moiety of the P2 ligand is also bridging the two metal centers. It coordinates the U ion in an η^2 fashion, with the U-C_{arene} distances (2.953(6) Å) in the range of those found in arene coordination complexes of uranium in higher oxidation states (3.189(2) Å- 2.692(3)), [15] and the Mo ion in an η^6 fashion. The Mo-C_{arene}(av) distances in **1** (2.25(2) Å) are shorter than those found in complex **B** (Mo1–C_{arene}(av)=2.304(3) Å) and similar to those found in the previously reported Mo(0) complex $[(N_2)MoP2]$, (Mo(0)-C_{arene}=2.255(1) Å) consistently with a lower oxidation state of Mo(0) in **1**, prone to significant metal-arene delta back-bonding interactions.[16] The arene C-C distances (avg. 1.425(8) Å) are elongated relative to free benzene, as expected, with C62-C63 being the longest (1.456(4) Å) due to interactions with two metals.

The coordination sphere of the Mo centre is completed by the two phosphine arms of the P2 ligand. The change in coordination mode of the P2 ligand from complex **B**, where only one of the phosphine groups binds the Mo, to the heterometallic nitride **1**, with both phosphines binding, is indicative of a change in the Mo-N interaction and oxidation state of the Mo centre.

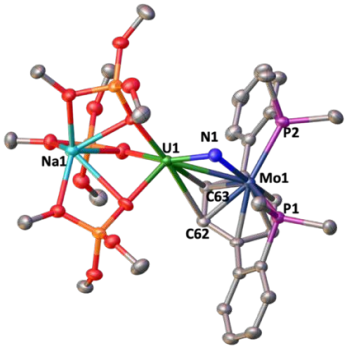

Figure 1. Solid-state molecular structure of **1** with thermal ellipsoids drawn at 50% probability level. The solvent molecules and the methyl groups of the *tert*-butyl and *iso*-propyl moieties have been omitted for clarity.

Overall, the metrical parameters of the solid-state structure of complex **1** are consistent with an asymmetric binding mode of the nitride U≡N-Mo resulting from a partial transfer of the nitride from the Mo centre to the U centre, concomitant with a two-electron transfer from the U to the Mo centre yielding a U(V)Mo(0) nitride. The preference of Mo to remain associated to the U-N fragment instead of dissociating and forming $[(N_2)MoP2]$ under N_2, indicates a relatively strong interaction with the nitride moiety. The absence of reaction between the Mo(IV) analogue [Cl(N)MoP2] with the U(III) complex **A** indicates that an electron rich, nucleophilic Mo(II) nitride is needed for coordination to U. The occurrence of a two-electron transfer and the presence of a U(V) ion was confirmed by EPR spectroscopy of **1** in solid state and frozen thf solutions**.** The X-band CW EPR spectrum of the powders of the UNMo complex **1** measured at 5 K (see Figure S28) exhibits a very intense transition centred d at g = 3.69, as well as a broader series of transitions centred at about $g \approx 0.59$.

The electron spin-echo (ESE) detected field-swept pulse EPR spectra (Figure S30) show no detectable spin echo signals in the region around g = 3.69, but the ESE-EPR intensity increases with the magnetic field and remains high at the maximum field achievable by our instrumentation (1458.5 mT), indicating that the species detected likely has principal g-values below g = 0.460. These signals are broadly consistent with a $j_z = \pm 5/2$ doublet ground state, and are similar to those previously reported for alkali bound terminal U(V) nitrides.[4b]

Hyperfine sublevel correlation (HYSCORE) spectroscopy[18] allows for detection of magnetic couplings of the paramagnetic uranium centre with NMR active nuclei which are too small to be resolved within the inhomogenously broadened CW-EPR spectrum.

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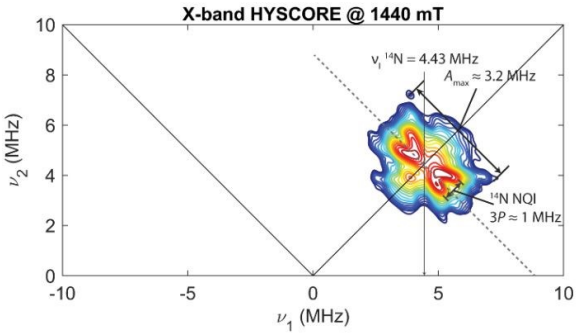
Field-dependent X-band HYSCORE spectra of **1** (Figure 2) exhibit signals consistent with a relatively weak coupling (A ≤ 3.2 MHz) to ^{14}N at all fields in the range from 1000 and 1440 mT. At the fields (and corresponding molecular orientations) accessible by our instrumentation, this ^{14}N coupling appears to have a very small to negligible isotropic component (a_{iso}), as only at the highest field achievable (1440 mT) it was possible to observe a clear splitting perpendicular to the diagonal of the (+,+) quadrant, as well as a small degree of splitting (~ 1 MHz) parallel to the diagonal due to the ^{14}N nuclear quadrupole interaction which further splits the nuclear spin sublevels. Combined, these field-dependent HYSCORE spectra indicate that the ^{14}N hyperfine tensor is primarily anisotropic, and at least at the orientations sampled within the field range accessible here, too small to correspond to a significant amount of spin density localized at the nitrogen s- or p-orbitals.

Figure 2. X-band HYSCORE spectrum of pure powder of 1 acquired at 1440 mT (g = 0.466).



These results suggest that HYSCORE techniques provide a versatile tool to investigate the nature of U-nitride bonding and spin distribution in U(V) compounds, as it has for a previous U(III) complex.[19]

In order to further analyse the binding mode in **1** we performed DFT studies. The geometry of **1** was achieved for three different spin states (doublet, quartet and sextet) and the doublet was found to have the lowest energy (see SI).

The optimized structure fits well the experimental one with the U-N bond distance of 1.83 Å (1.85 Å exp.), the U-O_{silox} distances in 2.24-2.26 Å range and the U-C_{arene} distances of 2.96 Å. The geometry around Mo is also satisfactorily reproduced with, for example, the N-Mo distance of 2.16 Å. The unpaired spin density for the ground state (U:1.2, N: -0.13 and Mo :-0.05, see SI) is in line with the presence of U(V) and a Mo(0) in the complex proposed based experimental structural parameters and EPR data. The bonding was thus analyzed using the Natural Bonding Orbital (NBO) analysis.

A triple bond U≡N is found and is polarized toward N (66% for the σ to up to 80% for the π, see SI). This polarized triple bond is in line with the obtained Wiberg Bond Index (WBI) found for the U≡N (2.26), indicative of some degree of covalency in the bond and it compares well with the U≡N WBI of 2.58 found in the Na-capped terminal uranium(V) nitride reported by Liddle.[4a, 20] This bonding is in accordance with the experimental analysis where the N-Mo interaction was expected to occur from a partial delocalization of the U-N interaction, in line with the presence of three (UN)-Mo 3c-2e bonds and N-Mo WBI of 0.73.

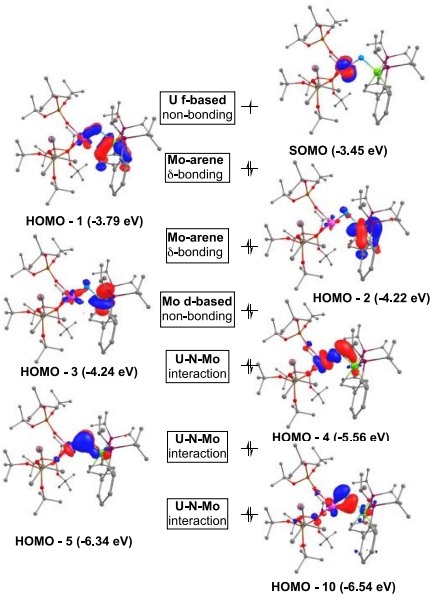


Figure 3. DFT Computed MOs for **1** indicating some U-N-Mo interactions (alpha spin data).

This description is further highlighted by scrutinizing the Molecular Orbital (MO) where three (UN)-Mo delocalized bonds are found in HOMO-4, HOMO-5 and HOMO-10 (Figure 3). This is further pointing in the direction of three (UN)-Mo 3c-2e bonds. Finally, at the second order donor acceptor a U-Mo interaction is observed as a donation from a lone pair of Mo occurs to an empty orbital of U (see table ST4 in ESI). This is in line with U…Mo WBI of 0.52, indicative of atomic orbital overlap and therefore of a bonding interaction. A similar interaction with a bond index of 0.56 was reported by Liddle in the heterometallic UMo phosphinoamide complex.[12]

Preliminary reactivity studies of **1** with ^{13}CO (1-10 equiv) show that reductive carbonylation of the nitride occurs leading to the formation of Na^{13}CO in 10-50% yield and previously reported Mo(0) carbonyl complexes, such as [P2Mo(^{13}CO)] or [P2Mo(^{13}CO)$_3$] (in low yield), as well as multiple unidentified diamagnetic species, as shown by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy (see SI).[16-17] The uranium species formed in the reaction could not be identified, but the formation of Na^{13}CO was unambiguously demonstrated by ^{13}C NMR spectroscopy of the reaction mixture in D_2O. Reports of nitride/CO coupling are scarce[21, 3b, 3e, 3f, 20] but include examples of terminal and bridging U(V) nitrides.[3b, 3h] The Mo binding to the U(V) nitride does not result in a reduced reactivity of the bridging nitride and reductive carbonylation of the U(V) nitride likely proceeds with release of the Mo(0) fragment, though direct reaction with **1** cannot be ruled out.

In summary we have shown that partial N-transfer from a nucleophilic Mo(II) terminal nitride to a U(III) can be used to isolate a heterometallic U nitride which provides the first example of a uranium-transition metal heterodimetallic nitride. Structural, EPR and computational studies indicate that N-

transfer is accompanied by a two-electron transfer from uranium to molybdenum and leads to a nitride triply bonded to U(V) and singly bonded to Mo(0). The isolated complex also shows a U-Mo interaction supported by the bridging nitride and the bridging arene ring of the P2 ligand. We anticipate that the presented synthetic method could be extended to other nucleophilic metal nitrides. Such heterometallic species are very attractive for further expanding the reactivity of metal nitrides.

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Conflicts of interest

There are no conflicts to declare

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