Multimetallic Uranium Nitride Cubane Clusters from Dinitrogen Cleavage

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ABSTRACT: Dinitrogen cleavage provides an attractive, but poorly studied route to the assembly of multimetallic nitride clusters. Here we show that the mono-electron reduction of the dinitrogen complex $[\{U(OC_6H_2\text{-}Bu^t_3\text{-}2,4,6)_3\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$, **1**, allows to generate for the first time a uranium complex presenting a rare triply reduced N_2 moiety ($(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)^{\bullet 3-}$). Importantly, the bound dinitrogen can be further reduced affording the U_4N_4 cubane cluster, **3**, and the U_6N_6 edged-shared cubane cluster, **4**, thus showing that the $(N_2)^{\bullet 3-}$ can be an intermediate in nitride formation. The tetranitride cluster showed high reactivity with electrophiles, yielding ammonia quantitatively upon acid addition and promoting CO cleavage to yield quantitative conversion of nitride into cyanide. These results show that dinitrogen reduction provides a versatile route for the assembly of large highly reactive nitride clusters, with U_6N_6 providing the first example of a molecular nitride of any metal formed from a complete cleavage of three N_2 molecules.

INTRODUCTION

Molecular nitride compounds were identified as important intermediates in the biological and industrial conversion of dinitrogen into ammonia and N-containing organic compounds, but the mechanism of N_2 cleavage to nitride remains unclear.[1-4] Because of their relevance as precursor and model of inorganic uranium nitrides and in the understanding of uranium-ligand multiple bonding, the chemistry of molecular uranium nitride compounds has witnessed significant advances in the last ten years.[5-6] The synthesis of molecular clusters analogues of uranium mononitride (UN) is important for modeling the properties of bulk UN, but most molecular uranium nitrides reported so far show a low nitride content (1 or 2 N^{3-} ligands)[7-26] [27] with only two larger U_4N_4 and U_8N_4 clusters containing 4 nitride ligands.[8, 28] Moreover, despite inorganic uranium compounds being reported to be efficient catalysts for N_2 conversion to ammonia,[29-30] only few examples of multimetallic uranium nitrides were so far prepared from dinitrogen cleavage (clusters **A-D** in Figure 1) [31-32, 28, 23-24] and only in one case intermediates containing less reduced N_2 species could be isolated.[28]

In general, the dinitrogen chemistry of molecular uranium compounds remains significantly less developed[33-35, 31, 36-44, 32, 28, 23] than *d*-block metals, with most complexes showing limited N_2 activation and identified as containing side-on bound doubly-reduced N_2. Further reduction of these systems was either not attempted or unproductive. Notably, in 2011, Arnold and coworkers[37] showed that the U(III) tris(aryloxide) complex $[U(OC_6H_3\text{-}Bu^t_2\text{-}2,6)_3]$, first reported by Sattelberger in 1988[45], and the tris-tert-butyl analogue $[U(OC_6H_2\text{-}Bu^t_3\text{-}2,4,6)_3]$ could react with N_2 under ambient conditions affording dinitrogen complexes. Spectroscopic, crystallographic and computational analysis of the $[\{U(OAr)_3\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$ complexes indicated that they

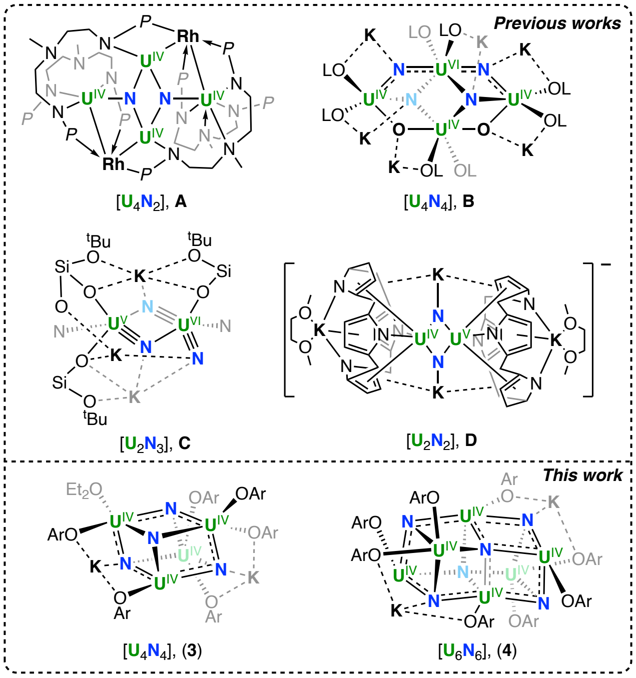
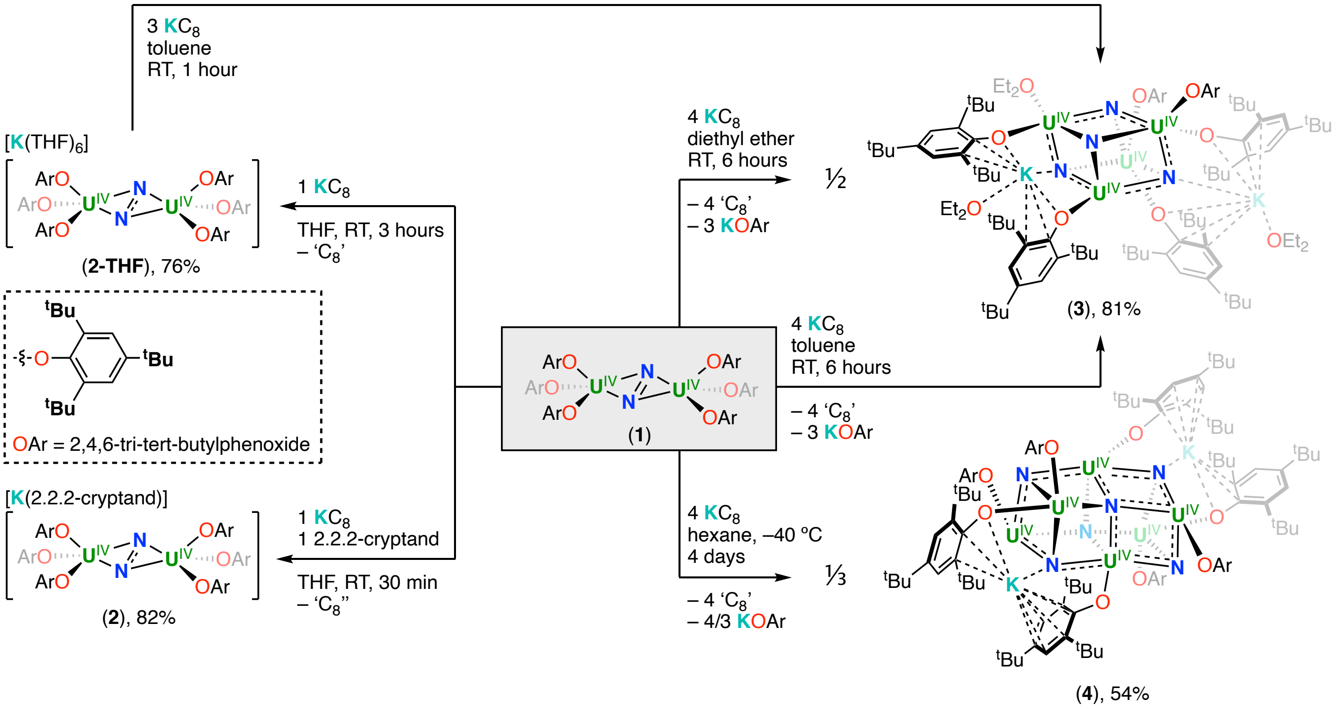


Figure 1. Examples of molecular uranium nitride clusters of different nuclearities obtained from N_2 cleavage (OL = $OSi(O^tBu)_3$, P = $P(^iPr)_2$, N = $N(SiMe_3)_2$, OAr = 2,4,6-^{t}Bu-C_6H_2O).

Scheme 1. Synthesis of the N_2-bridged complexes 2 and 2-THF, and of the tetranitride, 3, and hexanitride, 4, clusters from previously reported[33] complex 1.



were best described as containing two U(IV) f^2 centers bridged by a $(N{=}N)^{2-}$ ligand. A similar binding mode has been identified in a few other dinuclear complexes of uranium, showing variable stability with respect to N_2 release.[34-35, 38] An analogous $Ln_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ binding mode is also well known for cyclopentadienyl, aryloxide and amide dinitrogen complexes of lanthanides.[46-53, 39] Reduction of the bound dinitrogen in lanthanide[54] and in scandium complexes[55] was shown to yield mono-reduced radical- bridged $M_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)^{\bullet 3-}$ species that remain to date the only examples of isolated molecular compounds containing the $(N_2)^{\bullet 3-}$ moiety and which showed exciting single molecule magnet behavior.[56-59] Moreover, the $Sc_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)^{\bullet 3-}$ led to the first example of conversion a $(N_2)^{\bullet 3-}$–metal complex to N-containing organic compounds.[55] In contrast, preliminary attempts to reach higher N_2 reduction chemistry for the uranium trisaryloxide system by treating the complex $[U(OC_6H_3\text{-}Bu^t_2\text{-}2,6)_3]$ with an excess of reducing agent under N_2 only led to the isolation of the U^{III} 'ate' complex $K[U(OAr)_4]$.[37] Our group has recently reported dinuclear uranium complexes containing a tetra-reduced $(N\text{-}N)^{4-}$ ligand and demonstrated that the N-N bond can be further reduced and cleaved by controlled addition of reducing agent to yield a U_4N_4 cluster (Scheme 1) built from the cleavage of two N_2 molecules.[28] Motivated by these results, here we investigated the reduction of the previously reported dinitrogen complex $[\{U(OC_6H_2\text{-}Bu^t_3\text{-}2,4,6)_3\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$, **1** and were able to generate for the first time a uranium complex presenting a triply reduced N_2 moiety ($(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)^{\bullet 3-}$). Importantly, the bound dinitrogen could be further reduced affording U_4N_4 cubane and U_6N_6 edged-shared cubane clusters, thus showing that the $(N_2)^{\bullet 3-}$ can be an intermediate in nitride formation. Complex $[K_2\{U^{IV}_6(OAr)_8(\mu\text{-}N)_6\}]$, **4**, is the first example of a hexanuclear nitride cluster obtained by N_2 reduction and the largest nitride cluster obtained so far from dinitrogen cleavage.[60, 2]

RESULTS AND DISCUSSION

Synthesis of $N_2^{\bullet 3-}$-bridged diuranium complexes

Addition of 1 equiv. of KC_8 and 1 equiv. of 2.2.2-cryptand to a beige solution of the previously reported [37] U(IV)/U(IV) N_2 complex $[\{(ArO)_3U\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$, **1** in THF-$d_8$ at room temperature resulted in a color change to dark-brown and in the appearance of new ^1H NMR resonances at 77, 29, –7, –20 and –41 ppm, as well as full consumption of the starting material after 30 minutes (Figure S1). Dark-brown/black crystals of the reduced complex $[K(2.2.2\text{-cryptand})][\{(ArO)_3U\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$ (**2**) were obtained in 82% yield after 2 days from the filtered reaction mixture layered with hexane (Scheme 1). The molecular structure of **2** consists of an ion pair with the anionic complex $[\{(ArO)_3U\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$, presenting two uranium aryloxide moieties bridged by a side-on dinitrogen molecule (Figure 2). The N1-N1' bond distance at 1.425(5) Å is significantly elongated compared to that of the precursor N_2-complex **1** (1.19(2) Å – 1.236(5) Å) [37]. The value of the N-N bond distance is consistent with the reduction occurring at the bridging N_2 rather than at the metal center. Notably, similar values of N-N bond distances were reported for lanthanide N_2 complexes $[\{R_2Ln\}_2((\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2))]^-$ (1.396(7) Å – 1.402(7) Å for R = 2,6-^tBu-C_6H_2O; 1.401(6) Å – 1.405(3) Å for R = $(Me_3Si)_2N$); 1.362(9) Å – 1.392(9) Å for R = C_5Me_4H) containing a triply-reduced $N_2^{(\bullet 3-)}$ radical.[56-59] The U-O_{Ar} bond distances (2.222(4)- 2.252(4) Å) are only slightly longer than those found in the U(IV)/U(IV) $N_2(2–)$ precursor (2.170(6)- 2.095(6) Å).

To investigate the possible effects of coordinating alkali ions the reduction of **1** it was also performed in the absence of 2.2.2-cryptand. After the addiction of 1 equiv. of KC_8 to a beige solution of **1** in THF at room temperature the formation of dark-brown reaction mixture was observed (Figure S5). The complete reduction of the precursor was slower than in presence of cryptand and was complete only after 3 hours. The ^1H NMR spectrum of the reaction mixture showed the same signals as those obtained in presence of cryptand, suggesting that the alkali ion is not bound in solution. Crystals of $[K(THF)_6][\{(ArO)_3U\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$ (**2-THF**) suitable for X-ray diffraction were obtained in 76% yield after 3 days by layering the filtered reaction mixture with hexane. For both **2** and **2-THF,** exposure of the solids to dynamic vacuum freeze-thaw degassing their THF solutions did not result in loss of N_2 according to the ^1H NMR spectra.

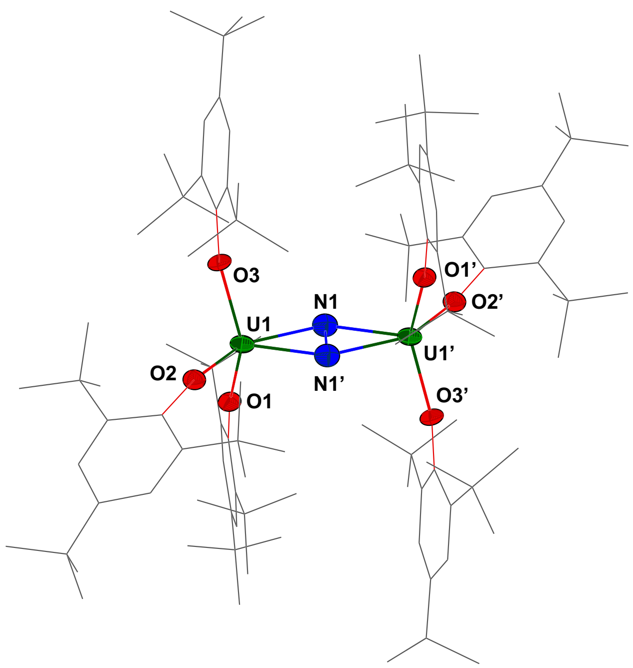


Figure 2. Molecular structure of the anionic unit $[\{(ArO)_3U\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]^-$ in **2**, with thermal ellipsoids drawn at the 50% probability level. Tris(tert-butyl)phenoxide ligands were depicted as wireframes for clarity. Hydrogen atoms and disordered tert-butyl groups were omitted for clarity.

Magnetic susceptibility data were collected for **2** in the range of 1.8 K to 300 K, under an applied DC field of 0.1 T (Figure S42-S45). Complex **2** possesses a large low-temperature magnetic moment of 3.6 μ_B per complex at 1.8 K, increasing upon warming up to 5.0 μ_B at 300 K (per complex, Figure S44). A steep drop to low values of the magnetic moment is often encountered with pure non-magnetic $5f^2$ non-Kramers U^{IV} ions, although an increasing number of U(IV) complexes deviating from this behavior were recently identified[61, 62, 63].

Neither χ vs. T nor χT vs. T plot demonstrate unambiguous features that could be associated with magnetic coupling of two U^{IV} ions through the radical bridge,[64] despite the high value of the measured magnetic moment.

As there are reports of U(IV)-radical compounds exhibiting SMM properties, [65] magnetization (M) *vs* field (H) measurements were performed, but no opening was observed in the M *vs* H curve (Figure S46). The magnetic moment values obtained for complex **2** (3.6 μ_B at 1.8 K and 5.0 μ_B at 300 K, per complex) are significantly higher than those measured for **1** (1.1 μ_B at 1.8 K, and 4.7 μ_B at 300 K, per complex) (Figure S52). The data recorded for **1** are consistent with the presence of two non-interacting U(IV) ions with a non-magnetic ground state (1.0 μ_B at 5 K and 3.4 μ_B at 300 K, per uranium center at 0.1 T).[66-67] The higher values of magnetic moment measured for **2** (2.6 μ_B at 5 K, 3.5 μ_B at 300 K per uranium center at 0.1 T, Figure S45) are likely due to a contribution from the ligand-centered radical and suggests that the anion $[\{(ArO)_3U\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]^-$ is best described as a U(IV)-$N_2(\bullet 3–)$-U(IV) species. These values are significantly higher than those found in charge separated monometallic U(IV) compounds with radical anionic ligands $[U^{IV}{-}(L\bullet{-})]$[68-70, 65] where the low-temperature (1.51−1.75 μB, 5 K, reported at 1 T) magnetic moments were assigned to magnetic contributions from the single unpaired electron of the radical ligand $[U^{IV}{-}(L\bullet{-})]$ as well as from the U^{III}/neutral ligand form $[U^{III}{-}L]$.[69-70, 65]

Variable-temperature X-band EPR measurements performed on frozen 2-methyltetrahydrofuran solutions of **2** showed that the complex is EPR-silent at room temperature as well as at 6 K. Similarly, the radical-bridged U(IV)/U(IV) diuranium complex $[\{((Me_3Si)_2N)_3U^{IV}\}_2(\mu\text{-bpym})][BPh_4]$, did not show any EPR signal at 6 K or at RT.[71] Several mononuclear uranium(IV) radical species, such as $[\{(SiMe_2NPh)_3\text{-tacn}\}U^{IV}(\eta^2\text{-}N_2Ph_2)]$[65] and $[((^{t\text{-}Bu}ArO)_3tacn)U^{IV}(\eta^2\text{-NNCPh}_2)]$ (tacn = 1,4,7-triazacyclononane)[72] also lack EPR features.

With the mono-reduced complex **2** on hand, we set out to investigate its reactivity and compare it with the N_2^{2-} complex **1**. The reactivity of the isolated complex **2** with protons was first explored. After the addition of excess HCl in diethyl ether, the complex yields 17% of NH_4Cl as measured by quantitative ^{1}H NMR experiment in DMSO-d_6 (Figure S27). In contrast, no ammonia was observed after addition of excess HCl to the U(IV)/U(IV) N_2-bridged complex **1** under the same conditions (Figure S26), suggesting a higher degree of activation of the bound dinitrogen in complex **2** compared to **1**.

However, complex **2** demonstrates no reactivity towards ^{13}CO at RT (1 eq., Figure S28-S29). This suggests that the degree of activation in **2** is lower compared to previously reported U(V)/U(V)-N_2^{4-} complexes [40-41] that reacted with ^{13}CO resulting in N-N cleavage and formation of NCO and CN^- or NCN^{2-} moieties, despite the similar N-N bond lengths observed in those species (1.425(5) Å for **2** compared to 1.521(18) Å and 1.40(1) Å for the nitrido- and oxo-bridged complexes, $[K_3\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}N)(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)\}]$ and $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}O)(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)\}]$, respectively).

In order to further investigate the reduction degree of N_2 in complexes **1**, **2-THF**, DFT calculations were carried out using the B3PW91 functional that has been successfully used to describe similar complexes in the past.[73] For complex **1**, three different spin states were computed and the quintet is found to be the ground state, with the triplet and singlet is being higher in energy (8.7 kcal/mol^{-1} and more than 45 kcal/mol^{-1}, respectively). The quintet spin state is in line with the presence of two U(IV) ions, and this is corroborated by the unpaired spin density located solely on the two uranium centers (Figure S55). That means that the central N_2 moiety is doubly reduced, which is in line with the N-N Wiberg Bond Index (WBI) of 1.92 (Fuzzy Bond Order, FBO, of 1.76) as well as the N-N distance of 1.23 Å (Table S6). This is very similar to the values found for the yttrium N_2 complex reported by Evans *et al.*[56] Indeed, in that system (Scheme S1) featuring the doubly reduced dinitrogen molecule, the N-N distance is 1.25 Å with a WBI of 1.98 (FBO 1.80) (Table S3).

The mono-reduced species **2-THF** were also investigated in the same way. Interestingly, two different types of structures were obtained with either an N-N bond still present, or with the one fully broken (Figure S65). The most stable structure is found to be the one in which the N-N bond is maintained, in line with the experimental isolation of complex **2-THF**. For this complex, three different spin states were computed, namely a doublet, quartet and sextet. The quartet and sextet were found to be lying at the same energy. The analysis of the unpaired spin density clearly shows that the two spin states exhibit the presence of unpaired spin density at the N_2 molecule (-0.96 for the quartet and +0.65 for the sextet) as also found for the yttrium $(N_2)^{\bullet 3-}$complex reported by Evans *et al*[56] (+0.65 for the high spin state), which would be in line with the formation of a $(N_2)^{\bullet 3-}$ and of two U(IV) moieties. The difference between the sextet and quartet is only in the coupling between the unpaired spins in $(N_2)^{\bullet 3-}$ and the two U(IV), which is antiferromagnetic for the quartet (negative value of the unpaired spin density) and ferromagnetic for the sextet (positive value of the unpaired spin density), as seen in the unpaired spin density plots (Figure S57-58). The N-N distance is around 1.34-1.37 Å and is elongated by more than 0.1 Å with respect to **1**. Finally, the N-N WBI is reduced to 1.20-1.30 (FBO 1.1-1.2) concomitant with the partial disruption of the N-N double bond (Table S8). For the sake of comparison, the reduced yttrium species were also found to exhibit unpaired spin density at the N_2 molecule in line with the formation of $(N_2)^{\bullet 3-}$ (Figure S54). The computed N-N distance is very similar to that found in **2-THF** (1.37 Å) and the N-N WBI is 1.27 (FBO 1.26), again similar to that found in **2-THF**.

Synthesis of uranium tetranitride and hexanitride clusters

Since the bound N_2 in **1** can be reduced with stoichiometric amounts of reducing agent, we then decided to investigate if further reduction was possible.

The reduction of **1** in diethyl ether with KC_8 (4 equiv. per U^{IV}/U^{IV} dimer) at room temperature produced over the course of 6 hours a black-purple solution and a white insoluble precipitate. When the solids (subsequently identified by ^{1}H NMR as KOAr) were filtered off and the reaction mixture was concentrated and placed at –40 ºC for one week, black crystals of the tetranitride cluster $[\{(Et_2O)K\}_2(Et_2O)U^{IV}{}_4(\mu\text{-}N)_4(OAr)_6]$, (**3**) formed in 81% yield.

The solid-state molecular structure of **3** shows the presence of a uranium-nitride molecular cube with uranium and nitrogen atoms on the vertices (Figure 3a). The uranium ions bind six aryloxide ligands in an uneven fashion (U3 and U4 bind each two aryloxide oxygens, while U2 and U1 bind only one aryloxide oxygen) with an overall aryloxide/uranium ratio of 1.5. In addition, one uranium atom (U1) also binds the oxygen atom from a diethyl ether molecule, with U-O_{ether} of 2.585(3) Å. Two inner-sphere potassium cations bind the nitride vertices N2 and N4 and also coordinate one ether molecule each.

The average value of the U-$N_{nitride}$ distance is 2.220 Å, which is in line with values reported for bridging nitrides in U(IV) complexes (2.012(16) –2.399(5) Å). [8, 27, 9, 74, 32]

The U-N bond lengths in **3** range from 2.169(3) Å to 2.258(3) Å (**Table S1**). The mean value of U-$O_{Ar.}$, at 2.263 Å is significantly longer compared to both **2** and **2-THF**, which can be associated with significant steric hindrance around the uranium/nitrogen core. The cubane structure found in **3** is unprecedented in uranium nitride chemistry, although an octa-nuclear triple-cubane structure $[(C_5Me_5)U(\mu^3\text{-}E)]_8$ (E = N or O) was identified by preliminary X-ray studies as the product obtained from the reduction of the metallocene precursor $[(C_5Me_5)_2U][(\mu\text{-}Ph)_2BPh_2]$ with KC_8 under N_2, and assigned as $[(C_5Me_5)U(\mu^3\text{-}N)]_8$ by DFT computation.[60] ^{1}H NMR studies showed that cluster **3** can also be cleanly prepared by reduction of **1** in toluene-d_8 at room temperature (Figure S7). Alternatively, cluster **3** can be obtained via reduction of **2-THF** with 3 equiv. of KC_8 in toluene, suggesting that reduction and subsequent splitting of the $(N_2)^{2-}$ moiety of **1** proceeds in a stepwise manner. Notably, when the reduction of **1** in diethyl ether was carried out with just 1 equiv. of KC_8 a few crystals of **3** where obtained, suggesting that reduction of a putative $(N_2)^{\bullet 3-}$ intermediate is faster than reduction of **1**.

Complex **3** was also investigated computationally by using the B3PW91 functional. The presence of a computationally stable structure with a fully broken N-N bond allows us to determine the energy needed to disrupt the N-N bond, and it is predicted to equal 24.7 kcal/mol^{-1} (required to form a doublet spin state, which would be bis-U(V) complex). This is indicating that in **2-THF** the nitrogen-nitrogen bond is weak enough to be fully broken by an excess of KC_8, as observed experimentally. Different spin states of **3** were investigated and the nonet is the ground state; it is a tetra-U(IV) cubane complex with the unpaired spin density only located on the uranium centers (Figure S62-S64). The averaged optimized U-N distance of 2.25 Å is in good agreement with the experimental structure (Table S10).

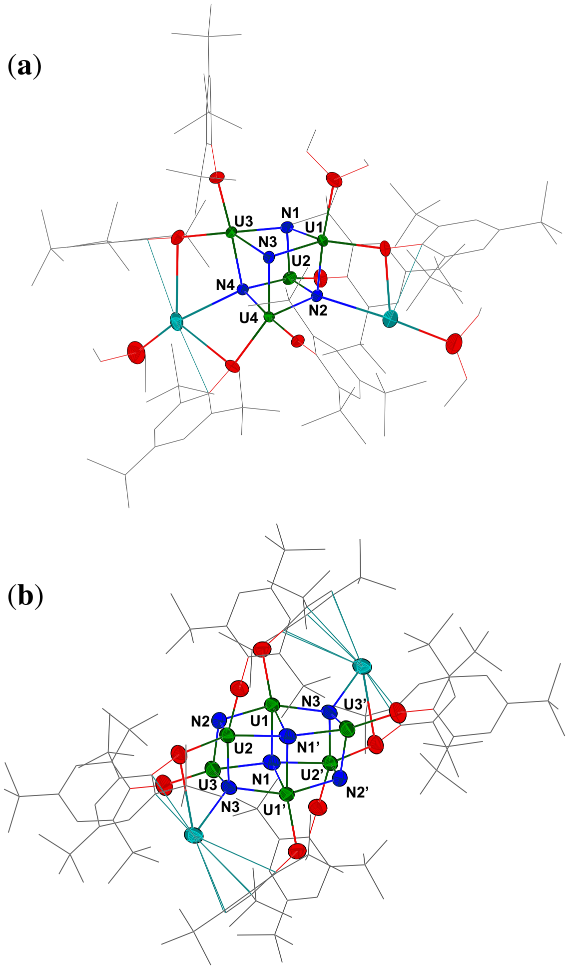


Figure 3. Molecular structures of the tetranitride $[\{(Et_2O)K\}_2(Et_2O)U^{IV}_4(\mu\text{-}N)_4(OAr)_6]$, **3**, (a) and of the hexanitride $[K_2\{U^{IV}_6(\mu\text{-}N)_6(OAr)_8\}]$, **4**, (b) with thermal ellipsoids drawn at the 50% probability level. Tris(tert-butyl)phenoxide ligands were depicted as wireframes for clarity. Hydrogen atoms and disordered tert-butyl groups were omitted for clarity.

To study the redox behavior of the N_2-aryloxide complex in a non-polar non-coordinating solvent, the reduction of **1** was also carried out in hexane. After the addition of 4 equiv. of KC_8 to **1** in hexane at –40 ºC, the color gradually changed to a darker shade of brown and the gold flakes of potassium graphite were consumed over the course of 96 hours. After leaving the filtered reaction mixture standing at –40 ºC for one week, dark-brown XRD-suitable crystals of the hexanitride cluster $[K_2\{U^{IV}_6(\mu\text{-}N)_6(OAr)_8\}]$, **4**, were obtained in 52% yield. The formation of **4** was also observed at room temperature but in much lower yield. The solid-state molecular structure of **4** shows the presence of a U_6N_6 fused dicubane core, eight aryloxide ligands and two potassium cations (Figure 3b). Two aryloxide ligands are binding the uranium centers U3 and U3', with every other uranium atom binding only one aryloxide resulting in an overall aryloxide/uranium ratio of 4/3.

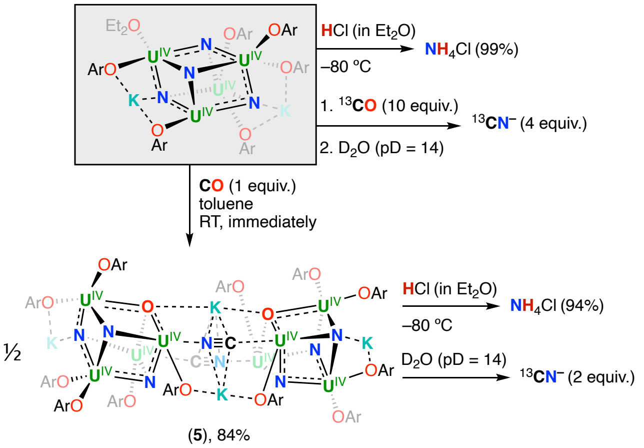
The formation of cluster **3** results from the reduction and subsequent cleavage of the bound dinitrogen from two molecules of **1**, and is accompanied by the loss of six equivalents of KOAr from two molecules of **1**. In contrast, the formation of **4** results from the combined N_2 cleavage and assembly of three complexes **1** and is accompanied by the loss of 10 equiv. of KOAr. It should be noted that no transformation of **3** to **4** was observed upon its solubilization in hexane. Notably, the hexanitride complex **4** represents the only unambigous example of a molecular nitride of any metal resulting from a complete cleavage of three N_2 molecules.[2]

These results demonstrated the important effect of solvent on the nuclearity and nitride content of uranium nitrides assembled from dinitrogen reduction. Recent relevant studies from Minasian, Arnold *et al.*[22] indicated that supporting ligand substituents could influence the nuclearity of nitrides obtained form azide reduction.

Reactivity studies

The reactivity of the isolated uranium tetranitride cluster **3** with protons and ^{13}CO was explored (Scheme 2). Upon the addition of excess HCl in diethyl ether to **3** 4 equiv. of NH_4Cl per complex formed (99% yield in NH_4Cl considering the formation of 4 equiv. of NH_4Cl per U_4N_4 cluster) as determined by ^1H NMR spectroscopy in DMSO-d_6, which confirms the presence of four nitride bridging groups (Figure S19). Quantitative formation (97%) of $^{15}NH_4Cl$ was also observed upon addition of excess HCl to the ^{15}N labelled analogue, **3-$^{15}N_2$** (Figure S20). Similarly, the hexanitride cluster **4** gave NH_4Cl in 96% yield (considering 100% as the formation of 6 equiv. of NH_4Cl per U_6N_6 cluster) after the addition of excess HCl in diethyl ether and ammonium chloride quantification (Figure S21).

Scheme 2. Reactivity of the tetranitride cluster with protons, and carbon monoxide affording the oxo/nitride cubane 5.



Moreover, the addition of 1 equiv. of ^{13}CO to **3** in toluene-d_8, resulted in a color change from purple to red and the ^1H NMR spectrum of the resulting solution showed full consumption of the starting material (Figure S17). Upon removing the volatiles and bringing the reaction mixture into hexane, single dark-purple-red crystals were isolated after 1 day at –40 ºC. The compound was identified as a CN-bridged cluster aggregate with the formula $[\{K\{U^{IV}_4(\mu\text{-}N)_3(\mu\text{-}O)\}(OAr)_6\}_2(\mu\text{-}K)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}CN)_2]$ (**5**). In this complex, two U_4N_3O cubane moieties are connected by two end-on CN groups, each bridging to two uranium atoms and two potassium cations (Figure 4a). Two additional potassium cations bind one nitride vertex of each cubane with a $N\cdots K_{bridging,\,av.} = 2.985$ Å (Table S1). The $C{\equiv}N_{bridging,\,av.}$ distance of 1.161 Å falls well within range of reported organic and bridging CN units and nitriles, including the diuranium complex $[Cs\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}CN)(\mu\text{-}O)\}]$, where $C{\equiv}N_{bridging}$ is 1.155(9) Å.[75] The overall cluster formula is consistent with the presence of 6 bridging nitrides and 2 bridging oxides formed from the cleavage of CO, but the crystallographic data do not allow to distinguish between O/N in the cluster core, probably due to the disorder of the oxygen atom over four different positions. Indeed, in both U_4N_3O cores (Figure 4b) all atoms are equivalent (U–N/O$_{nitrido/oxo,\ av.}$= 2.258 Å) and the bond variation is narrow with U–N/O$_{nitrido/oxo,\ shortest}$ = 2.199(2) Å and U–N/O$_{nitrido/oxo,\ longest}$ = 2.298(3) Å, comparable to the U-N$_{nitrido}$ distances found in **3** (2.169(3) Å – 2.258(3) Å), longer than the U-O$_{oxo}$ distances (2.157(2) Å and 2.089(2) Å) found for triply bridging oxides in the tetranuclear bis-nitride bis-oxo cluster $[K_4\{(OSi(O^tBu)_3)_2U^{IV}\}_2\{(OSi\text{-}(O^tBu)_3)_2U^{V}\}_2(\mu^4\text{-}N)_2(\mu\text{-}O)_2(\mu^3\text{-}O)_2]$[28] but shorter than the average U–μ^4-O distance (mean value 2.36(3) Å) found in U(IV) oxo clusters.[76]

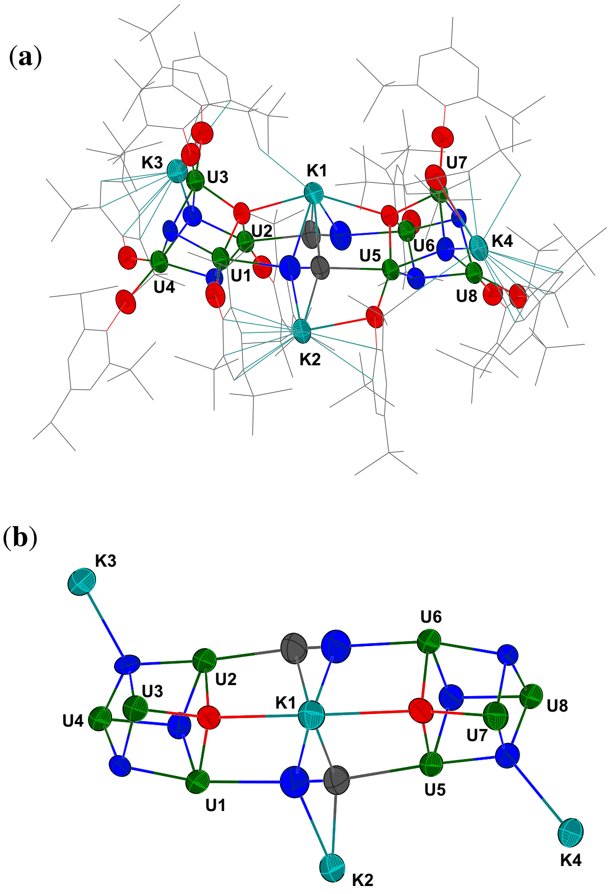


Figure 4. Molecular structure of $[\{K\{U^{IV}_4(\mu\text{-}N)_3(\mu\text{-}O)\}(OAr)_6\}_2(\mu\text{-}K)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}CN)_2]$, **5** (a), and of the $[\{U_4N_3O_2K_2\}_2(K)(CN)_2]$ core in **5** (b), with thermal ellipsoids drawn at the 50% probability level. Tris(tert-butyl)phenoxide ligands were depicted as wireframes for clarity. All hydrogen atoms and disordered tert-butyl groups were omitted for clarity. The bridging oxide position was assigned in arbitrary fashion.

Upon addition of HCl in diethyl ether to **5**, the formation of six equivalents of NH_4Cl (94%) per molecule of cluster were detected by ^{1}H NMR in DMSO-d$_6$ (Figure S25), confirming the presence of six nitrides in **5**. Moreover, ^{13}C NMR studies of a sample of crystalline **5** quenched in basic (pD = 14) D_2O revealed the presence of $^{13}CN^-$ (Figure S18), and carbon-13 quantification performed on the reaction mixture after the addition of 1 equiv. of ^{13}CO showed the formation of 1 equiv. ^{13}CN per single U4 unit, thus confirming the nature of the bridging group in **5** (Figure S24).

The molecular structure of **5** indicates that the reaction of **3** with CO results in the cleavage and deoxygenation of two molecules of CO by two bridging nitride N groups, resulting in the substitution of two nitrides by two oxides groups without disruption of the structure.

The addition of excess CO to the tetranidride cluster resulted in the slow formation of different reaction mixtures as indicated by ^{1}H NMR studies, with a complete transformation taking up to 1 week. The transformation is accompanied by a change of color of the reaction mixture from dark-purple/black to light-yellow and disappearance of ^{1}H NMR resonances assigned to **3** (Figure S22). Quantitative ^{13}C NMR studies of the reaction mixtures obtained after the reaction of the tetranitride cluster **3** with excess (10 equiv.) ^{13}CO at room temperature for a week, performed after quenching in basic D_2O (pD = 14), showed the presence 4 equiv. of $^{13}CN^-$ per starting tetranitride complex (Figure S23). This demonstrates that all four nitrides react with CO effecting its deoxygenative cleavage.

CONCLUSION

In summary, we have shown that the bridging side-on N_2 ligand in dinuclear uranium complexes can be reduced stepwise by an external reducing agent in a controlled manner. One-electron reduction led to the isolation of the first example of a diuranium complex of the ($N_2^{\bullet 3-}$) radical moiety. Further reduction of the ($N_2^{\bullet 3-}$) species led to the assembly of cubane clusters with high nitride content (U_4N_4 and U_6N_6), with the nuclearity of the cluster being controlled by the nature of the solvent. The tetranitride cluster showed high reactivity with electrophiles yielding ammonia quantitatively upon acid addition, as well as promoting CO cleavage to give quantitative conversion of nitrides to cyanides. These results show that dinitrogen reduction provides a versatile route for the assembly of large nitride clusters with high reactivity and indicate that ($N_2^{\bullet 3-}$) species can also serve as possible intermediates in the conversion of N_2 to nitrides. Moreover, U_6N_6 provides the first example of a molecular nitride of any metal resulting from a complete cleavage of three N_2 molecules.

ASSOCIATED CONTENT

Supporting Information

X-ray data for complexes **2-5** (CIF), and additional crystallographic details, experimental procedures, ^{1}H NMR spectra, SQUID data and computational details (PDF).

The Supporting Information is available free of charge on the ACS Publications website.

Accession codes

CCDC 2295064 (complex **2**); 2295065 (complex **2-THF**); 2295066 (complex **3**); 2295067 (complex **4**); 2258011 (complex **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

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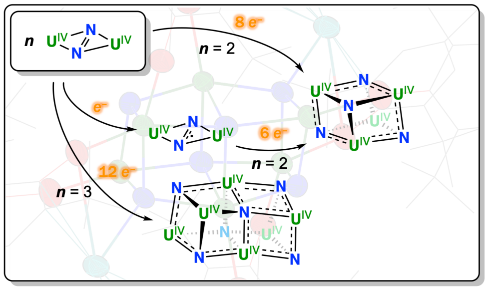
Graphical abstract



Uranium **N**itride cubane clusters from N_2 cleavage