Progress in Molecular Uranium-Nitride Chemistry

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Abstract

The coordination, organometallic, and materials chemistry of uranium nitride has long been an important facet of actinide chemistry. Following matrix isolation experiments and computational characterisation, molecular, solution-based uranium chemistry has developed significantly in the last decade or so culminating most recently in the isolation of the first examples of long-sought terminal uranium nitride linkages. Herein, the field is reviewed with an emphasis on well-defined molecular species.

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1. Introduction

Investigations into the chemical bonding and reactivity of actinide elements are vital for developing future nuclear applications, ameliorating existing legacy waste issues, as well as furthering our fundamental understanding of the f block elements.¹ In the past two decades, non-aqueous chemistry has undergone a rapid expansion,²⁻⁴ in particular multiple bonds concerning U=O ,⁵⁻¹⁴ U=N ,^{6,9,15-41} and U=E (E = S, Se, Te)^{12,42} have been investigated with great interest. Furthermore recent developments into U=C multiple bonds means they now represent a burgeoning field of research.^{17,43-57} However, due to the prominent paucity of reports of formal $\text{U}\equiv\text{N}$ triple bonds in uranium nitrides significant attention focussed on the isolation of a terminal uranium-nitride linkage in order to address the lack of knowledge of its intrinsic physicochemical properties.

Uranium mononitride has long been considered a suitable material for Generation IV fast spectrum nuclear reactors such as the gas-cooled, lead-cooled and sodium-cooled fast reactors as well as new concepts for light-water reactors.^{58,59} Binary UN is regarded a

superior candidate over uranium oxide fuels due to its higher melting point ($\sim 2850\text{ }^{\circ}\text{C}$), higher thermal conductivity and advantageously increased density (14.32 g cm^{-3}).⁶⁰

Uranium nitride exists in three stoichiometric ratios; UN, U_2N_3 and UN_2 . U_2N_3 can be synthesised from uranium metal and N_2 at $850\text{ }^{\circ}\text{C}$, and subsequent decomposition to binary UN is achieved *via* further heating to $1150\text{ }^{\circ}\text{C}$.⁶¹ A number of techniques have been developed to produce uranium nitride from UO_2 . The most common of these is carbothermic reduction, which despite extensive research still requires expensive infrastructure and, due to relatively high carbon and oxygen content, often results in contamination by impurities.⁶²⁻⁶⁶ Alternatively, sol-gel methods have been utilised to synthesise UN. There have also been reports of these two techniques being applied in conjunction.⁵⁹ Less energetically demanding routes have been proposed by reacting UC or UF_4 with ammonia, however synthetic routes utilising UO_2 or uranium metal are more feasible on industrial scales due to the extent by which they are available, both commercially and naturally.⁶⁷⁻⁶⁹ A relatively economical technique compared to carbothermic reduction has been developed, where UN is synthesised *via* ball-milling of uranium metal with N_2 to afford high purity UN.⁵⁸ However, despite the research conducted in this area the synthesis of UN and study of the bonding and reactivity of the $\text{U}\equiv\text{N}$ fragment remains largely unexplored. As a result, significant attention has been focussed on utilising molecular precursors and matrix isolation experiments to probe the nature of uranium nitrides.

2. Spectroscopic Isolation of Uranium Nitrides

Figure 1 – Spectroscopically Studied Molecular Nitrides

2.1. UN and NUN

In 1976 Green and Reedy first observed UN as part of an argon matrix isolation infra-red (IR) study. At 14 K uranium atoms were produced by a hollow cathode sputtering device with argon (Ar) which was subsequently exposed to low concentrations of N₂ (0.05 % in Ar) or NO₂. Upon annealing, an absorbance at 1001 cm⁻¹ was observed which was attributed to UN. In addition, a tentative assignment of 1051 cm⁻¹ was given to the ν_3 absorption of NUN.⁷⁰ In 1993 Andrews and co-workers examined the reactivity of laser ablated uranium atoms with molecular nitrogen in an Ar matrix at 12 K. The only product formed was determined to be linear NUN which was characterised through ν_3 absorption at 1051 cm⁻¹ and this was confirmed by isotopic labelling which supported the previous observation by Green. Although IR inactive ν_1 modes are predicted to arise at 1008 cm⁻¹, the absence of such bands suggests linearity within these species. The NUN molecule is synthesised through uranium atom insertion into a single N₂ molecule and the reaction is enhanced by UV (ultraviolet) photolysis which helps overcome the activation energy for reaction. At high N₂ concentrations the nitrogen complexes UN₂-N₂ and UN₂-(N₂)₂ were identified by ν_3 absorbances at 1041 and 1032 cm⁻¹, respectively.⁷¹ An extension of this work was reported in 1998 identifying two previously unreported uranium nitrides, U(μ -N)₂U and NU(μ -N)₂U (for IR absorbances see Table 1), which can be detected through laser ablation of uranium in condensing pure N₂ as minor products along with the major product of NUN. Quasirelativistic density functional theory (DFT) calculations revealed predicted ground states for UN and NUN of ⁴ Σ and ¹ Σ_g , respectively. Bond lengths for UN and NUN of 1.746 and 1.717 Å, respectively, were calculated wherein NUN exhibits a linear geometry in agreement with other theoretical results.^{72,73} Viswanathan conducted a similar matrix isolation study and reported that increasing concentrations of N₂ yielded increasing amounts of UN. It was therefore suggested that at high N₂ concentrations new reaction channels are generated through the formation of N· and N₃ radicals which can react with uranium atoms or NUN to yield UN.⁷⁴

Compound	U $\equiv$ N ¹⁴ cm ⁻¹	U $\equiv$ N ¹⁵ cm ⁻¹
UN	1001	969
UN ₂	1051	1019
UN ₂ (N) ₂	1041	1010
UN ₂ (N ₂) ₂	1032	1001
	670	648
U(μ -N) ₂ U	580	562
NU(μ -N) ₂ U	968	938
NU(μ -N) ₂ U	844	817
NUO	984	953
[NUO] ⁺ [NO] ⁻	1017	987
NUF ₃	938	-
NUNH	967	937
22	955	930
23	936	900
27	914	883
31	856	827

Table 1 - Experimentally observed IR U $\equiv$ N absorbances and isotopomer shifts.

2.2. NUO

In 1997 Andrews and co-workers investigated the reactivity of laser ablated uranium towards NO in argon matrices at 6-7 K. This reaction predominantly formed the insertion product NUO which exhibits characteristic IR absorption bands at 984 (U-N) and 819 cm⁻¹(U-O). Quasirelativistic DFT calculations supported the assignment and predicted a linear geometry and a ² Φ electronic ground state. Also characterised in this report is the uranyl analogue [NUO]⁺[NO]⁻.⁷⁵ NUO and [NUO]⁺ have also been isolated in neon matrices whilst [NUO]⁺ has been observed in the gas phase through mass spectrometry.^{76,77} Collision-induced-dissociation experiments and ligand exchange reactions resulted in the identification of [NUO]⁺ from the exothermic reaction of UN⁺ (generated from U⁺ + NO₂) with O₂, CO₂ SO₂ and COS. The study also deduced the heat of formation for [NUO]⁺ to be $\Delta H_f^\circ = 145.6 \pm 29.2$ kcal mol⁻¹ and theoretical calculations conducted by Pyykkö and Schwarz predicted the U-N bond distances to be shorter in comparison to the U-O bond lengths.^{76,78} NUN and [NUO]⁺ are isoelectronic analogues of the [UO₂]²⁺ dication and thorough computational studies have been conducted on the species, deducing that the U-N bonding in NUN and [NUO]⁺ is significantly more covalent than in the U-O bonding exhibited in [UO₂]²⁺ and [NUO]⁺.⁷⁹

2.3. $EU\text{F}_3$ ($E = \text{N or P}$)

The terminal nitrido and phosphido molecules NUF_3 and PUF_3 have been observed using IR spectroscopy in the reaction of laser-ablated uranium atoms with EF_3 ($E = \text{N, P}$). The $\text{U}\equiv\text{N}$ vibrational absorbance was assigned to a band at 938 cm^{-1} , whilst $\text{U}\equiv\text{P}$ was not observable. *Ab initio* studies support the assignment of the IR bands for these species with calculated bond lengths for $\text{U}\equiv\text{N}$ and $\text{U}\equiv\text{P}$ of 1.76 and 2.40 Å (CASPT2) and effective bond orders of 2.78 and 2.40, respectively. The studies also calculated the $\text{U}\equiv\text{N}$ bonding in NUF_3 to be stronger and more covalent (460 kJ mol^{-1}) than the $\text{U}\equiv\text{P}$ bonding in PUF_3 (176 kJ mol^{-1}) demonstrating that the U 5f orbitals achieve greater orbital overlap to N than P, therefore bonding more effectively with the smaller, harder nitrogen ligand.⁸⁰

A further study by Andrews reported the exposure of laser-ablated uranium atoms to N_2 and H_2 in an argon matrix at 5 K. Aside from the formation of NUN and UN , the new uranium(V) nitride imide molecule $\text{N}\equiv\text{U}=\text{NH}$ was characterised through the identification of one N-H (3350 cm^{-1}), two U-N stretching modes ($\text{U}\equiv\text{N} = 967\text{ cm}^{-1}$, $\text{U}=\text{N} = 752\text{ cm}^{-1}$) and one UNH bending mode (433 cm^{-1}) in the IR spectrum of NUNH .⁸¹ These assignments were fully supported by isotopic labelling studies. It is proposed that initially formed NUN reacts under UV irradiation with hydrogen atoms to form $\text{N}\equiv\text{U}=\text{NH}$. Although not isolated, the mixed azide/nitride species NUN_3 has been investigated using computational calculations. This complex was calculated to be stable in the singlet and triplet states and linear with a calculated $\text{U}\equiv\text{N}$ bond distance of 1.73 Å.⁸² In addition, Gagliardi and Pyykkö theoretically investigated the metal actinide nitrido species $[\text{NUOs}]^-$, NUIr , $[\text{NUPt}]^+$ and $[\text{NUAu}]^{2+}$ as analogues to uranyl. Calculations in the singlet and triplet states gave $\text{U}\equiv\text{N}$ bond lengths of 1.76, 1.72, 1.69 and 1.68 Å, respectively, and each molecule exhibits the electronic ground state and first excited state of $^1\Sigma^+$ and $^3\Phi$, respectively. Of most significance is the neutral molecule NUIr . Calculations suggest two strong triple bonds involving σ - and π -components, which would therefore be isoelectronic with NUN and uranyl. A synthetic route was also proposed towards the isolation of NUIr using either simultaneous evaporation of the three elements, or to start with the diatomic species IrN or UN .⁸³ The synthesis of these simple

uranium nitride complexes, albeit at very low temperatures under exotic experimental conditions, led to many attempts to synthesise the terminal uranium nitride linkage under ambient conditions and only very recently has this challenge been successfully been met.

3. Molecular Uranium Nitrides

3.1. Attempts with Nitride Transfer Reagents and Dinitrogen Activation

Initial attempts to synthesise the terminal nitrido functionality were reported by Cummins and co-workers in 2000. Reaction of the nitride transfer reagent Li(dbabh) (Hdbabh = 2,3:5,6-dibenzo-7-azabicyclo[2.2.1]hepta-2,5-diene) with $[\text{UI}_3(\text{THF})_4]$ did not yield the expected uranium nitride product as is observed analogously for chromium.⁸⁴ Instead, the uranium(V)-hexakisamido complex $[\text{Li}(\text{THF})_x][\text{U}(\text{dbabh})_6]$ was isolated and characterised.⁸⁵ Cummins subsequently reported that mixing trivalent U^{III} and Mo^{III} precursors, $[\text{U}(\text{THF})\{\text{N}(\text{tBu})\text{Ar}\}_3]$ (**1**) ($\text{Ar} = 3,5\text{-C}_6\text{H}_3\text{Me}_2$) and $[\text{Mo}\{\text{N}(\text{R})\text{Ph}\}_3]$ [$\text{R} = \text{tBu}$ or Ad (Ad = 1-adamantyl)], under an N_2 atmosphere yielded the heterodinuclear complex $[\text{U}\{\text{N}(\text{tBu})\text{Ar}\}_3(\mu\text{-}\eta^1:\eta^1\text{-N}_2)\text{Mo}\{\text{N}(\text{R})\text{Ph}\}_3]$ (**2**) ($\text{R} = \text{tBu}$, Ad) and not the expected N-N cleavage product (Scheme 1). Complex **2** exhibits an N-N bond length of 1.232(11) Å that is significantly longer than in free N_2 suggesting reduction to an $[\text{N}_2]^{2-}$ unit, whilst the uranium-amide bond lengths are consistent with tetravalent uranium(IV). It is proposed that the dinitrogen complex $[\text{Mo}\{\text{N}(\text{R})\text{Ph}\}_3(\text{N}_2)]$ is initially formed but trapped by the strongly Lewis acidic uranium complex, generating the observed dinuclear product.⁸⁶

Scheme 1 – Synthesis of $[\text{U}\{\text{N}(\text{R})\text{Ar}\}_3(\mu\text{-}\eta^1:\eta^1\text{-N}_2)\text{Mo}\{\text{N}(\text{R})\text{Ph}\}_3]$, **2**.⁸⁶

3.2. Bridging Uranium Nitrides

The first uranium nitrido complex to be isolated in any significant quantity was synthesised *via* the reductive cleavage of dinitrogen. Despite several reports of uranium dinitrogen bonding, this report by Gambarotta is still the only complex to effect dinitrogen cleavage and nitride formation.⁸⁷⁻⁹² Treatment of $[\{\text{Et}_8\text{-calix(4)tetrapyrrole}\}\text{U}(\text{DME})][\text{K}(\text{DME})]$ (**3**) with $\text{K}(\text{C}_{10}\text{H}_8)$ under an N_2 atmosphere afforded the mixed-valent dinuclear $\text{U}^{\text{IV}}/\text{U}^{\text{V}}$ μ -nitrido complex $[\{\text{K}(\text{DME})(\text{Et}_8\text{-calix[4]tetrapyrrole})\text{U}\}_2(\mu\text{-NK})_2][\text{K}(\text{DME})_4]$ (**4**), Scheme 2. The $\text{U-N}_{\text{nitride}}$ bond lengths of 2.076(6) and 2.099(5) Å, Figure 2, are comparable to uranium nitrogen double bonds⁴ and the nitride source (N_2) was confirmed through isotopic labelling studies.⁹³

Scheme 2 – Synthesis of $[\{\text{K}(\text{DME})(\text{Et}_8\text{-calix[4]tetrapyrrole})\text{U}\}_2(\mu\text{-NK})_2][\text{K}(\text{DME})_4]$, **4**.⁹³ Ethyl substituents and $[\text{K}(\text{DME})_4]$ are omitted for clarity.

Figure 2 - Molecular structure of the anion of **4**, hydrogen atoms and ethyl groups have been removed for clarity.

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Figure 3 - Molecular structure of 6 with hydrogen atoms omitted for clarity.

Scheme 4 - Synthesis of $[\{\text{Cp}^*\text{U}(\mu\text{-I})_2\}_3(\mu_3\text{-N})]$, 7.⁹⁵

Figure 4 - Molecular structure of 7 with hydrogen atoms omitted for clarity.

Evans has also investigated the reductive capacity of $[\text{Cp}^*\text{UI}_2(\text{THF})_3]$ towards sodium azide. The resultant product was a trinuclear uranium cluster featuring bridging iodide ligands and a μ_3 -nitrido centre, $[\{\text{Cp}^*\text{U}(\mu\text{-I})_2\}_3(\mu_3\text{-N})]$ (**7**) ($\text{Cp}^* = \text{C}_5\text{Me}_5$) (Scheme 4 and Figure 4) synthesised through the reduction of azide by U^{III} centres in 33% yield. However, X-ray crystallographic techniques cannot discern the nitride from an oxide or indeed a hydroxide which may be present as a result of the presence of adventitious oxygen.⁹⁵ A collation of U-Cp and U-I bond distances for known U^{III} and U^{IV} complexes was studied to ascertain the oxidation state of the uranium centres. However, unfortunately this could not provide unambiguous confirmation. Consequently, isotopic labelling studies analysed by atmospheric pressure chemical ionisation mass spectrometry were conducted which deduced the central atom was indeed nitrogen. This was confirmed when the oxide complex, synthesised separately, proved to have different analytical properties (NMR, space group, colour).⁹⁶ Support for this formulation was provided through extensive DFT and CASPT2 analysis which calculated the uranium spin densities to be equivalent and therefore U^{IV} . As a consequence, this provides evidence to support the assertion that the central atom is indeed a nitride. The experimental $\text{U-N}_{\text{nitride}}$ bond lengths of 2.138(3), 2.152(3) and 2.157(3) Å are consistently shorter than known amido bond lengths and agree well with the calculated bond distances. Also reported was the tentative identification of a further polymetallic species, $[\text{Cp}^*\text{U}(\mu_3\text{-E})]_8$ (E = N, O) (**8**), from the reaction of **5** with KC_8 under N_2 , Scheme 5. X-

ray crystallographic techniques could not reliably identify E as oxide or nitride and further characterisation (NMR, mass spectrometry, elemental analysis, isotopic labelling) could not be conducted. DFT and CASPT2 analysis predicted both molecules to be stable. However, experimental values are more consistent with a tetravalent uranium cluster in which E is a nitride centre based on comparison to calculated U-N bond lengths.⁹⁷

Scheme 5 – Synthesis of $[\text{Cp}^*\text{U}(\mu_3\text{-E})]_8$ (E = N, O), **8**.⁹⁷

Scheme 6 - Synthesis of $\{[\text{Cs}(\text{MeCN})_3][\text{U}_4(\mu_4\text{-N})(\mu\text{-N}_3)(\text{MeCN})_8\text{I}_6]\}_x$, **9**.⁹⁸

Nitrido cluster chemistry has also been investigated by Mazzanti and co-workers. The group synthesised the heptaazide tetravalent precursor complex $\text{Cs}_3[\text{U}(\text{N}_3)_7]$ with a view to subsequent nitride formation. Treatment with $[\text{UI}_3(\text{THF})_4]$ yielded the nitrido-azido tetrametallic cluster $\{[\text{Cs}(\text{MeCN})_3][\text{U}_4(\mu_4\text{-N})(\mu\text{-N}_3)(\text{MeCN})_8\text{I}_6]\}_x$ (**9**) (Scheme 6).⁹⁸ The nitrido centre of **9** bridges four uranium centres and exhibits U-N_{nitride} bond lengths ranging 2.271(3) to 2.399(5) Å, Figure 5. The compound is a result of a two-electron

reduction of an azide by two U^{III} centres. It is important to note that to date this is the only isolated molecular nitride which is not stabilised by sterically demanding ancillary ligands; it is proposed the nitrido centre provides an important role in the cluster formation, acting as a template.

Figure 5 – Molecular Structure of 9, with only the uranium-nitrido core shown for clarity.

The exploitation of the reductive capacity of trivalent uranium to facilitate two-electron redox chemistry with azides has been an area of extensive research in the field of uranium imido complexes. In general the reduction of organic azides (RN_3) with uranium results in the formation of $\text{U}=\text{NR}$ complexes.^{15,16,18,19,21,26,29} Consequently, research turned to inorganic azides as a source of nitrido synthons. Cummins reported the first example of a nitridoborate complex of uranium in 2009, Scheme 7. Treatment of **1** with $[\text{N}^n\text{Bu}_4][(\text{N}_3)\text{B}(\text{C}_6\text{F}_5)_3]$ afforded the borane-capped pentavalent uranium nitrido complex, $[\text{N}^n\text{Bu}_4][\{(\text{C}_6\text{F}_5)_3\text{BN}\}\text{U}\{\text{N}^n(\text{tBu})\text{Ar}\}_3]$ (**10**) with concomitant evolution of N_2 in 80% yield.⁹⁹ The complex features a linear $\text{U}-\text{N}-\text{B}$ [$177.8(3)^\circ$] unit, Figure 6, and exhibits a $\text{U}-\text{N}_{\text{nitride}}$ bond length of $1.916(4) \text{ \AA}$ which is comparable with the $\text{U}-\text{N}_{\text{imido}}$ distance observed in $[(\text{Me}_3\text{SiN})\text{U}(\text{N}'')_3]$ [$1.910(16) \text{ \AA}$] [$\text{N}'' = \text{N}(\text{SiMe}_3)_2$].¹⁸ Interrogation of **10** by

cyclic voltammetry revealed that a reversible one-electron oxidation process to the hexavalent complex was potentially accessible. This oxidation was achieved chemically through the use of 0.5 equivalents of I_2 or one equivalent of AgOTf to form $[\{(C_6F_5)_3BN\}U\{N(tBu)Ar\}_3]$ (**11**) in 82% yield. The oxidation results in a contraction of the U-N_{nitride} bond length by 0.04 Å to 1.880(4) Å whilst retaining linearity [B-N≡U = 179.4(3)°]. The complex also exhibits a lengthening of the B-N bond length upon oxidation from 1.540(6) Å in **10** to 1.592(6) Å in **11**. This is one of the shortest U-N bonds to be reported in a molecular context. However, attempts to cleave the N-B bond to furnish a terminal uranium nitride complex have thus far proved unsuccessful.

i) + $[N^tBu_4][\{(N_3)B(C_6F_5)_3\}]$, - N_2 , THF. ii) + 0.5 I_2 , - $[N^tBu_4][I]$. iii) + 0.5 MN_3 , - N_2 .

iv) + 0.5 AgOTf, - 0.5 Ag, $1/2$ MOTf. v) 0.5 $[Cp_2Fe][B(Ar^F)_4]$, - 0.5 Cp_2Fe .

M = Na, N^tBu_4 . Ar = 3,5-Me₂C₆H₃. Ar^F = 3,5-(CF₃)₂C₆H₃.

Scheme 7 – Synthesis of 10–14.^{99, 100}

Figure 6 – Representative structures of the uranium nitrides **11 and **13** with hydrogen atoms omitted for clarity.**

Shortly following this work attempts to synthesise uranium nitride complexes using unprotected azides were reported by Cummins, Scheme 7. Straightforward addition of MN_3 ($M = Na, N^tBu_4$) to **1** provided the bimetallic U^{IV} complex $[M][(\mu-N)\{U[N^tBuAr]_3\}_2]$ (**12**) in good yield.¹⁰⁰ The neutral mixed valent $U^{IV/V}$ complex $[(\mu-N)\{U[N^tBuAr]_3\}_2]$ (**13**) was generated through reaction with $AgOTf$ and further oxidised to the cationic $U^{V/V}$ monovalent compound $[(\mu-N)(U\{N^tBuAr\}_3)_2][B(Ar^F)_4]$ (**14**) [$Ar^F = 3,5-(CF_3)_2C_6H_3$] by treatment with $[Cp_2Fe][B(Ar^F)_4]$. A study of the redox chemistry of **13** supplied evidence for strong communication between the uranium centres with a $K_c \approx 5.6 \times 10^{17}$ for the comproportionation of $[U=N=U]^-$ and $[U=N=U]^+$. In addition, X-ray crystallographic studies of these three complexes, Figure 6, revealed a decrease in the $U-N_{(nitride)}$ distances per one-electron oxidation with $U-N$ bond lengths of 2.079(av), 2.0625(2) and 2.049(av) Å for **12**, **13** and **14** respectively. The contraction of the $[U=N=U]$ core was assigned to an increase in electrostatics as a result of the removal of non-bonding electrons. The reaction chemistry was also investigated. Addition of $NaCN$ to **14** formed the previously reported dinuclear cyanoimide complex $[(\mu-$

NCN){U(N[^tBu]Ar)₃]₂}]¹⁰¹ through a two-electron reduction and insertion into the nitride bridge by the cyanide anion.

Scheme 8 - Synthesis of 15 - 17.¹⁰²

Despite reports of *bis*(imido) (RN=U=NR) uranium complexes,¹⁰³⁻¹⁰⁵ derivatives of the uranyl analogue, in particular the [NUO]⁺ ion, were not isolated and reported until 2010 by Hayton. A two-electron reduction of NaN₃ by two equivalents of [UN''₃] generated the tetravalent species [Na(DME)₂(TMEDA)][(N'')₂U(μ-N)(CH₂SiMe₂NSiMe₃)U(N'')₂] (**15**) (Scheme 8) in 69% yield. Although this reduction of azide was not unprecedented, the unexpected deprotonation of a methyl group yielded a μ-CH₂ group and liberated HN''. The U-N_{nitride} bond lengths (1.95(1) and 2.12(1) Å), Figure 7, are not equivalent, which suggests localised U-N=U interactions which may be a result of the acute U-N=U bond angle of 123.5(5)°. Further oxidation to the neutral U^(IV/V) complex [(N'')₂U(μ-N)(CH₂SiMe₂NSiMe₃)U(N'')₂] (**16**) with iodine revealed an even greater separation in U-N_{nitride} distances of 1.909(6) and 2.201(6) Å, Figure 8, providing additional evidence for localised bonding. The reaction of **15** with Me₃NO produced the U^{VI} mono-oxo complex [Na(DME)₂][(N'')₂U(μ-N)(CH₂SiMe₂NSiMe₃)U(N'')₂(=O)] (**17**) in 84 % yield, Scheme 8. The sodium capped oxo ligand coordinated *trans* to the nitride ligand is reminiscent of the [O=U=N]⁺ cation and provides evidence for the high degree of multiple bonding U^{VI} can offer. The complex exhibits a U-O bond distance of 1.797(7) Å and a contracted U^{VI}-N_{nitride} bond length of 1.818(9) Å, Figure 9. In contrast, the U^{IV}-N_{nitride} bond lengthens to 2.284(8) Å and is thus 0.47 Å longer than U^{VI}-N_{nitride} distance supporting the localised bonding proposal. Investigations into possible magnetic coupling between the uranium

centres in **15** and **16** using SQUID magnetometry revealed no observable communication which is likely due to the localised bonding scheme.¹⁰²

Figure 7 - Molecular structure of $[\text{Na}(\text{DME})_2(\text{TMEDA})][(\text{N}''_2)\text{U}(\mu\text{-N})(\text{CH}_2\text{SiMe}_2\text{NSiMe}_3)\text{U}(\text{N}''_2)]$, **15. Hydrogen atoms and cationic component are omitted for clarity.**

Figure 8 - Molecular structure of $[(\text{N}''_2)\text{U}(\mu\text{-N})(\text{CH}_2\text{SiMe}_2\text{NSiMe}_3)\text{U}(\text{N}''_2)]$, **16. Hydrogen atoms are omitted for clarity.**

Figure 9 - Molecular structure of $[\text{Na}(\text{DME})_2][(\text{N}'')_2(\text{O})\text{U}(\mu\text{-N})(\text{CH}_2\text{SiMe}_2\text{NSiMe}_3)\text{U}(\text{N}'')_2]$, **17**. Hydrogen atoms are omitted for clarity.

3.3. Photochemically Generated Uranium Nitrides

The decomposition of azide complexes *via* photolysis has proved an advantageous route towards transition metal nitrido complexes,¹⁰⁶⁻¹⁰⁸ however initial investigations into the photolysis of uranium azides did not result in activation of the azide group.¹⁰⁹ In 2010 Kiplinger, Batista and co-workers reported the photolysis of a series of tetravalent terminal uranium azide complexes, Scheme 9, prepared using a gold azide transfer reagent.^{110,111} In the case of $[\text{Cp}^*_2\text{U}(\text{N}_3)(\text{NR})]$ [$\text{R} = \text{NPh}_2$, $\text{O}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$] photolysis led to decomposition or unidentifiable products. In contrast, photolysis of $[\text{Cp}^*_2\text{U}(\text{N}_3)(\text{N}'')]$ (**18**) resulted in the isolation of the mixed amide complex $[\text{Cp}^*(\text{C}_5\text{Me}_4\text{CH}_2\text{NH})\text{U}(\text{N}'')]$ (**19**) (Scheme 9 and Figure 10).¹¹² The decomposition of azide upon photolysis was observed by IR spectroscopy with the subsequent growth of an N-H band. The complex exhibits a U-NH bond length of 2.129(3) Å consistent with reported U^{IV} amide bond distances.¹¹³

Scheme 9 – Synthesis of 19 and 20.¹¹²

Figure 10 - Molecular structure of 19. Hydrogen atoms except for the amide hydrogen are omitted for clarity.

DFT calculations conducted on $[Cp^*_2U\{N(SiH_3)_2\}(N_3)]$ found the formation of $[Cp^*(C_5Me_4CH_2NH)U\{N(SiH_3)_2\}]$ was an exergonic process releasing $36.2 \text{ kcal mol}^{-1}$ free energy. The decomposition of azide was found to be as a result of high energy MLCT transfer observed at 17500 cm^{-1} in the UV/vis/NIR spectrum between uranium and azide ($f \rightarrow \pi^*$) leading to N_2 loss and hexavalent uranium nitride formation. Selective

irradiation UV/vis/NIR experiments confirmed the need of UV/vis photolysis rather than NIR, in promoting activation of the azide and the high energies required for reaction. The pathway by which C-H activation occurs from nitride was investigated by DFT analysis of the possible intermediates. The lowest energy route was found to involve deprotonation of the methyl group by nucleophilic attack of the nitride unit to generate a U^V imido transition state, followed by subsequent 1,2-migration of the methylene group to yield U-NH-C linkage, Scheme 10. Formally the $U\equiv N$ linkage inserts into a C-H bond in a 1,1-fashion. This type of nitride reactivity is unprecedented for f-element and transition metals yet reminiscent of cytochrome P450 oxidation of C-H bonds to alcohols. The high reactivity and nucleophilicity of the nitride unit is exemplified by the low selectivity observed upon photolysis of analogous $[(Cp^{Me_4Et})_2U(N_3)(N'')]$ which afforded a mixture of the possible products $[(Cp^{Me_4Et})(C_5Me_4CH_2CH_2NH)U(N'')]$ and $[(Cp^{Me_4Et})\{C_5(Me)_3(Et)(CH_2NH)\}U(N'')]$. Attempts to trap the transient terminal uranium nitride using Lewis acidic capping groups such as $B(C_6F_5)_3$ were conducted. Photolysis of a 1:1 mixture of **18** and $B(C_6F_5)_3$ resulted in the isolation of the borane-capped azido species $[\{Cp^*_2U(N'')\}(\mu-\eta^1:\eta^1N_3)\{B(C_6F_5)_3\}]$ (**20**) which is photolytically inactive and can be reversibly converted back to **18** through dissolution in THF. This seminal work suggests terminal uranium nitrides are feasible, yet highly reactive.

Scheme 10 – C-H activation pathway of uranium(VI) nitride.¹¹²

3.4. Terminal Uranium Nitrides

Recent work reported by Liddle has described the isolation of the terminal uranium nitride linkage for the first time utilising a highly sterically encumbered ligand framework, Scheme 11. In a two-electron redox reaction, treatment of $[U(Tren^{TIPS})]$ (**21**) ($Tren^{TIPS} = N(CH_2CH_2NSi^iPr_3)_3$) with NaN_3 in pyridine afforded, following work up, the pentavalent dinuclear complex, $[U(\mu-N)(\mu-Na)(Tren^{TIPS})]_2$ (**22**).¹¹⁴ The complex exhibits

a relatively short U-N_{nitride} bond length of 1.883(4) Å, and the nitride groups are mutually stabilised by bridging sodium cation interactions. The observed ¹⁴N/¹⁵N isotopomer shift for the U≡N IR band from 955 to 930 cm⁻¹ (calculated shift 925 cm⁻¹), supports the nitride source and formulation. Sequestration and encapsulation of the sodium cations through straightforward addition of two equivalents of 12C4 (12-crown-4) to **22** yielded the first uncapped terminal uranium(V) nitride complex, [U(N)(Tren^{TIPS})]⁺[Na(12C4)₂]⁻ (**23**) (Scheme 11). An X-ray diffraction study conducted on the complex revealed a U-N_{nitride} bond length of 1.825(15) Å in the terminal complex, Figure 11, which is ~0.06 Å shorter than in the bridging species. IR isotopic labelling studies (UN = 936 cm⁻¹, U¹⁵N = 900 cm⁻¹), electronic absorption spectroscopy, and magnetic measurements support the formulation.

Scheme 11 - Synthesis of **22** and **24**.¹¹⁴

DFT calculations demonstrated that the HOMO-1, -2 and -3 represent significant U≡N interactions in which one σ - and two π -components are present. The σ interaction is higher in energy than the quasi-degenerate π components with similar MO ordering to the uranyl dication,¹¹⁵ but the reverse of U=C and U=N bonding manifolds. NBO analysis revealed significant uranium contributions to the σ - and π -components (32 and 27%, respectively) and significant participation of the 5f orbitals (44 and 72%, respectively)

with variable 6d contributions (47 and 28%, respectively) and a Mayer bond index of 2.91 was calculated for the $\text{U}\equiv\text{N}$ triple bond. Preliminary studies into the reactivity of the nitrido unit have also been conducted. Treatment of **23** with Me_3SiCl yielded the pentavalent terminal imido uranium species $[\text{U}(=\text{NSiMe}_3)(\text{Tren}^{\text{TIPS}})]$ (**24**), Scheme 11, which could be prepared independently from **21** and Me_3SiN_3 , which suggests a nucleophilic nitride that contrasts to the reactivity observed for **13**. Notably, **23** decomposes in ethereal solvents which is consistent with the previous paucity of terminal uranium nitrides. Also, addition of H_2O under reducing conditions liberated ammonia confirming a basic nitride functionality.

Figure 10- Molecular structure of **23**. Hydrogen atoms are omitted for clarity.

Scheme 12 – Synthesis of 25-29.¹¹⁶

Very recently, Liddle has reported the isolation of a terminal uranium(VI) nitride, Scheme 12.¹¹⁶ Initial attempts to oxidise **22** with mild oxidants such as iodine or AgPF₆ resulted in loss of the nitride linkage and the formation of uranium(IV)-iodide or -fluoride derivatives **25** and **26** as the only isolable species. However, treatment of **23** with iodine resulted in clean oxidation and after removal of the [Na(12C₄)₂][I] by-product afforded [U(N)(Tren^{TIPS})] **27**. The IR spectrum of **27** exhibits a U≡N stretch at 914 cm⁻¹ (883 cm⁻¹ for the U¹⁵N isotopomer; calculated shift to 885 cm⁻¹) which compares well to **23** (Table 1). The U-N_{nitride} bond length of 1.799(7) Å, Figure 12, is now very short but is only modestly contracted compared to **23** (1.825(15) Å) which may reflect the fact that a non-bonding 5f-electron is removed upon oxidation.

Figure 12 – Molecular structure of **27**. Hydrogen atoms are omitted for clarity.

Interestingly, **27** is less stable than **23**, and in solution **27** was found to convert into the cyclometallated, C-H activated product **28** in a reaction that is analogous to the chemistry that produces **19** reported by Kiplinger and Batista.¹¹² The conversion of **27** into **28** was found to be promoted by strong sunlight ($t_{1/2} \sim 7$ days) but accelerated by photolysis using a 125 W medium-pressure mercury lamp to be complete in 20 minutes at room temperature. This experimentally corroborates the computational proposal of Kiplinger and Batista that **19** is produced from a transiently formed nitride intermediate. Indeed, the formation of **28** suggests an important reason for the prior absence of terminal uranium(VI) nitrides since photolysis of an azide to nitride functional group was a previously identified strategy for producing a uranium nitride. In-line with this, photolysis of compound **29** results in clean conversion to **28**. It is thus concluded that photolysis of uranium azides can produce uranium nitrides, but under photolytic conditions subsequent C-H activation and insertion occurs to afford amide derivatives. In contrast, photolysis of **23** does not result in amide formation, which demonstrates the greater stability of the uranium(V) nitride linkage over the uranium(VI) nitride linkage.

This is entirely consistent with the mechanism in Scheme 10 since the first step after azide conversion to nitride is facile electron transfer to uranium which would be favoured for uranium(VI) over uranium(V) since the former is more oxidising than the latter.

Scheme 13 – Synthesis of **30** and **31**.¹¹⁶

The recent isolation of uranium(V) and (VI) nitrides raised several questions about why the $\text{U}\equiv\text{N}$ linkage had been so elusive and Liddle has reported reactivity data which provide some explanations. It is clear that a very bulky ancillary ligand was required that provided a pocket for azide to react with **21**, yet was sterically demanding enough to prevent the newly installed nitride bridging to another uranium centre as observed, for example, in **10-17**. The presence of a stabilising sodium ion in the synthesis of **22** would appear to be key since when **21** is treated with $[\text{Bu}_4\text{N}][\text{N}_3]$ the primary amido complex **30** is formed, Scheme 13 and Figure 13. This suggests a nitride is formed transiently, but without the electrostatic stabilisation provided by sodium during installation the nitride reacts with solvent; this was confirmed by a deuterium labelling study which confirmed the two amide hydrogen atoms in **30** originate from the toluene solvent of reaction.

Figure 13 – Structures of **30** and **31**. Hydrogen atoms are omitted for clarity.

The abstraction of the sodium ions was also investigated. Whereas covalently bound boranes (cf **10-14**, **19**) and trimethylsilyl groups (cf **24**) remain impervious to removal from the nitride functional group, the electrostatically bonded sodium ions in **22** can be sequestered by 12C4 to give **23**. However, it was reported that a range of crown ethers and cryptands fail to abstract the sodium ions from **22**, which presents further evidence of the nucleophilic nature of the terminal uranium nitride linkage, and treating **22** with 15C5 (15-crown-5 ether) results in the monomeric complex **31** where the nitride is still coordinated to sodium, Scheme 13 and Figure 13. Crystallographic analysis of complex **31** showed a U-N_{nitride} bond length of 1.810(5) Å which is surprisingly similar to **23** and **27**. The characterisation data for **31** support the pentavalent formulation, and the IR data show a UN stretch at 856 cm⁻¹ which is reduced to 827 cm⁻¹ for the ¹⁵N-isotopomer (reduced mass calculation predicts 829 cm⁻¹). Thus, the identity of the sodium sequestering agent appears to be a key factor in the successful isolation of a terminal uranium nitride. The isolation of **27** from **23** but not **22** shows that the method of oxidation is important, and the stability of uranium(V) vs (VI) nitrides shows that the oxidation state of uranium has a profound effect on the stability of the terminal uranium nitride linkage.

These recent advances have enabled a computational assessment of the nature of the uranium nitride bond. Computational analysis of **27** is surprising inasmuch as there is very little variation in the composition of the $\text{U}\equiv\text{N}$ triple bond between the (V) and (VI) oxidation states of uranium. However, a consistent theme is that the σ -component is always higher than the π -components for nitrides, as is the case for uranyl, whereas the corresponding imido complexes follow the normal energetic ordering of $\pi > \sigma$ as is the case for $\text{U}=\text{C}$ double bonds. This energetic ordering is proposed to occur in nitrides due the unusually short U-N distance manifesting an antibonding interaction between a σ -orientated nitrogen p-orbital overlapping with the toroidal 5f and 6d lobes on uranium. A QTAIM study of these nitrides and isovalent group 6 nitrides suggested the surprising conclusion that the levels of covalency in uranium nitride bonds is of similar, if not greater, magnitude to group 6 nitrides.

4. Summary and Outlook

It is clear that the field of uranium nitride chemistry is now burgeoning. After elegant matrix isolation experiments and computational characterisation methods led the way, and threw down the gauntlet to the synthetic actinide community, significant advances in uranium nitride chemistry have been made in the last decade or so. Many molecular bridging uranium nitrides have now been isolated and thoroughly characterised. More recently, the first terminal uranium(V) and (VI) nitrides have at long last been secured. These advances have provided significant insights into the bonding of the $\text{U}\equiv\text{N}$ triple bond suggesting that a rich seam of novel reactivity is awaiting discovery. Several questions now present themselves. What is the scope of ligand-sets that can stabilise uranium nitride linkages? Can terminal uranium nitrides with uranium in the (III) and (IV) oxidation states be isolated? Given the novel reactivity and magnetism that can be supported by Tren-uranium complexes,^{88,117-120} what stoichiometric and catalytic reactivity might be achieved with terminal uranium nitride linkages? Given the patent for Haber Bosch ammonia synthesis mentions uranium and uranium nitrides as efficient promoters of ammonia formation,¹²¹ what relevance do the molecular systems described herein have to their heterogeneous congeners? Could molecular systems such as the ones

described herein constitute useful low-temperature precursors to uranium nitride materials? Further research into this area in order to fully understand the nature of the $\text{U}\equiv\text{N}$ triple bond is surely warranted.

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ToC Entry

The chemistry of molecular uranium nitrides is reviewed.

Highlights

- Uranium nitride matrix isolation experiments reviewed.
- Aspects of uranium nitride materials chemistry and applications reviewed.
- Molecular bridging uranium nitrides reviewed.
- Photochemical approaches to terminal uranium nitrides reviewed.
- Molecular terminal uranium nitrides reviewed.