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Back bonding without σ-bonding: a unique π-complex of dinitrogen with uranium

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Abstract

The synthesis, molecular structure, spectroscopic properties and bonding in a complex of dinitrogen with trivalent uranium are described. The molecule has a side-on U–N_2–U core which is supported by U → N_2 π donation with no significant N_2 → U bonding. Steric compression between the spectator triamidoamine ligands prevents the uranium atoms from approaching the N_2 ligand at the optimum distance for overlap, and thus the N–N distance is not displaced significantly from that in gaseous dinitrogen. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Back bonding; π-Complexes; Uranium; Dinitrogen

1. Introduction

In recent years there has been a intense interest in dinitrogen coordination, activation and fixation by transition metal centres [1]. Highlights include the metal-mediated splitting of the N–N bond [2], and the intramolecular reaction of coordinated N_2 with H_2 [3]. Despite the inability of lanthanide centres to participate in significant covalent bonding to ligands, the reactivity of dinitrogen with complexes of these elements is now surprisingly well established [4]. Complexes of dinitrogen with actinide elements are exceedingly rare [5,6].

Our contribution to the chemistry of triamidoamine [7] $N(CH_2CH_2NR)_3$ complexes has concentrated on the lanthanide [8,9] and actinide systems [10,11]. For uranium, the majority of compounds have contained U(IV), although a few other situations have arisen, such as in the mixed valence (III/IV) bimetallic $[\{U(NN'_3)\}_2\text{-}\mu\text{-Cl}]$ [12] [$NN'_3 = N(CH_2CH_2NSiMe_2Bu^t)_3$]. The U(III) and U(IV) components of this compound may be separated by fractional sublimation (Eq. (1)) [5].

$$[\{U(NN'_3)\}_2\text{-}\mu\text{-Cl}] \rightarrow [U(NN'_3)] + [U(NN'_3)Cl] \quad (1)$$

In this report we describe the reaction of the complex $[U(NN'_3)]$ toward dinitrogen and a discussion of the bonding situation in the product. Part of this work has been communicated [5,13].

2. Results and discussion

2.1. Synthesis of $[\{U(NN'_3)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$ (**1**)

When a sample of $[U(NN'_3)]$ in benzene-d_6 was placed under ca. 1 atm of rigorously dry dinitrogen a colour change from purple to red occurred and new peaks appeared in the ^{1}H-NMR spectrum corresponding to a species with a threefold symmetry on this timescale. Increasing the pressure to slightly above 1 atm led to essentially complete conversion to a new species **1** (Scheme 1). Increasing the temperature of the sample led to a shift in the equilibrium toward $[U(NN'_3)]$ as might be expected. Partially replacing the dinitrogen in the headspace with pure dihydrogen had a similar effect and no new species (except H_2) were detected. When a sample containing **1** was freeze–thaw degassed, the intense purple colour and ^{1}H-NMR spectrum of **1** were again observed. Exposure of saturated pentane solu-

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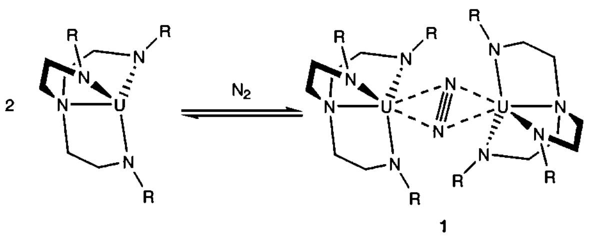

Scheme 1. Reversible formation of **1**.

tions of $[\mathrm{U(NN'_3)}]$ to dinitrogen and cooling to −20°C gives dark red crystals of analytically pure $[\{\mathrm{U(NN'_3)}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}\mathrm{N_2})]$ (**1**).

The molecular structure of **1** (Fig. 1) shows that the dinitrogen ligand is bound in a side-on bridging mode between two uranium centres. The (triamidoamine)uranium fragments are of approximate trigonal monopyramidal geometry and are arranged in a mutually staggered conformation as found for $[\{\mathrm{U(NN'_3)}\}_2\text{-}\mu\text{-}\mathrm{Cl}]$ [12]. The uranium atoms sit out of the planes defined by the three respective amido nitrogen atoms by ca. 0.84 and 0.85 Å. The apical amino N–U bond lengths of 2.555(5) and 2.601(5) Å are unexpectedly short compared to those in tetravalent $\mathrm{UNN'_3}$) complexes (ca. 2.7 Å) [11] and in $[\{\mathrm{U(NN'_3)}\}_2\text{-}\mu\text{-}\mathrm{Cl}]$ [2.78(2) Å] [12]. The U–N(dinitrogen) bond distances of between 2.39 and 2.44 Å, are rather longer than typical U–N(amido) bonds of ca. 2.28 Å. in contrast, the Sm–N bond lengths in $[\{\mathrm{Cp^*_2Sm}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}\mathrm{N_2})]$ [4] are similar to those observed in Sm(III)–$\mathrm{NR_2}$ compounds [14]. The N–N bond length in **1** of 1.109(7) Å is essentially the same as that found in dinitrogen gas (1.0975 Å) [15] (vide infra).

As is expected for this symmetric complex, $^{14}\mathrm{N_2}$-**1** and $^{15}\mathrm{N_2}$-**1** gave superimposable IR spectra. We have thus far been unable to obtain reliable Raman spectra of these isotopomers due to their thermal and other instability.

The UV–vis spectrum of **1** is very similar that of trivalent $[\mathrm{U(NN'_3)}]$, with intense broad bands typical of trivalent uranium complexes. If the addition of dinitrogen to $[\mathrm{U(NN'_3)}]$ had led to an increase in the oxidation state of the uranium centre we would expect a very significant change in this spectrum [16].

The magnetic susceptibility of the Curie–Weiss magnet $[\mathrm{U(NN'_3)}]$ was measured in toluene-d_8 solution in an atmosphere of argon by the Evans method [17] and found to be 3.06 BM between 225 and 295 K. The sample was then freeze–thaw degassed and exposed to a slight overpressure of dinitrogen. The clean conversion to **1** was confirmed by ^{1}H-NMR spectroscopy as before. The magnetic susceptibility of the sample was then found to be only marginally increased giving a magnetic moment of 3.22 BM per uranium atom in the same temperature range. The magnetic susceptibilities of triamidoamine complexes of uranium appear to be somewhat insensitive to changes in formal oxidation state, but we can say that this value is consistent with the presence of either uranium(III) or uranium(IV) but not uranium(V) which in this system would normally have a $\mu_{\mathrm{eff}} < 2.2$ BM [18].

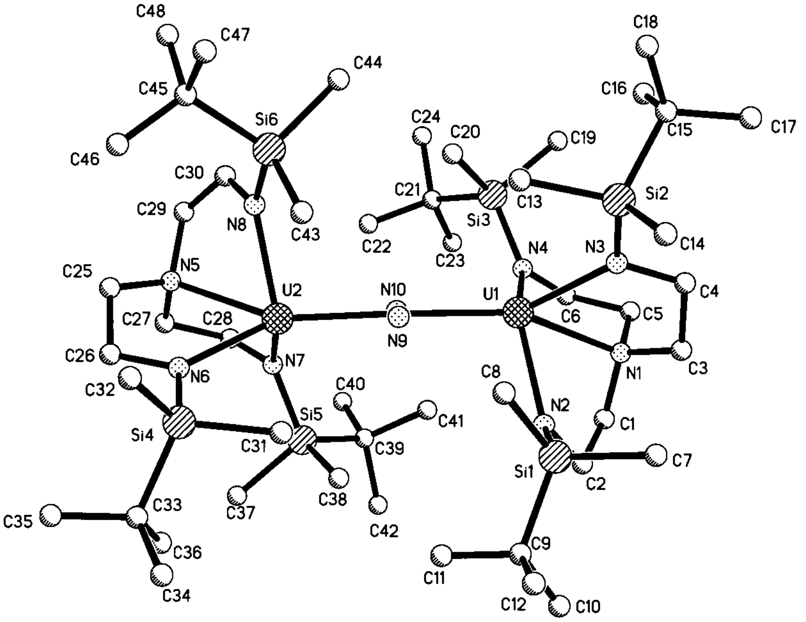

Fig. 1. Thermal ellipsoid plot of the molecular structure of $[\{\mathrm{U(NN'_3)}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}\mathrm{N_2})]$ (**1**); hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): N(9)–N(10) 1.109(7), U(1)–N(9) 2.394(5), U(2)–N(9) 2.397(5), U(1)–N(10) 2.439(5), U(2)–N(10) 2.446(5), U(1)–$\mathrm{N_2}$ 2.352, U(2)–$\mathrm{N_2}$ 2.357, U(1)–N(1) 2.555(5), U(1)–N(2) 2.279(5), U(1)–N(3) 2.289(5), U(1)–N(4) 2.291(5), U(2)–N(5) 2.601(5), U(2)–N(6) 2.284(4), U(2)–N(7) 2.281(5), U(2)–N(8) 2.265(5), U(1)–$\mathrm{N_2}$–U(2) 2.7.

Taking into consideration that the dinitrogen ligand in **1** is clearly not in a highly reduced state, and also noting the signature U(III) UV spectrum, we propose that coordination of dinitrogen to [U(NN$'_3$)] leads to no change in the valency of the uranium centre. In contrast, ^{13}C-NMR spectroscopic data for [{Cp$^*_2$Sm}$_2$(μ-η^2:η^2-N$_2$)] are consistent with the presence of Sm(III) centres [4]. Similarly, tetravalent [{Mo(NN$'_3$)}$_2$(μ-N$_2$)] contains a diazenido (N_2^{2-}) ligand and hence molybdenum (IV) [19]. Cummins has reported a reaction of a mixture of molybdenum and uranium(III) amides with dinitrogen to give a fascinating group of end-on bound Mo(μ-N$_2$)U complexes in which both metal centres have a formal oxidation state of +4 [6]. The uranium(III) amide used does not independently react with dinitrogen, but is coaxed into the interaction by precoordination of N$_2$ at the more strongly π-donating Mo centre.

2.2. Bonding between U and N$_2$ in 1

The bonding in f element complexes is often regarded as being essentially ionic in nature on the basis that f orbitals are core like and unable to overlap effectively with ligand functions. This is arguably well justified for 4f systems; for example the coordination numbers and geometries in many classical lanthanide complexes are often poorly defined in solution as the metal exerts little or no electronic control over the spatial arrangement of the ligands. This lack of covalency also extends to organometallic lanthanide systems, for example there does not appear to be significant M → L π-donation in lanthanide complexes such as [Cp$^*_2$Yb(η^2-MeCCMe)] [20]. That this lack of covalency extends to the actinide series is, however, much more debatable; indeed the physicochemical properties of certain actinide systems cannot be satisfactorily explained without invoking appreciable metal–ligand covalency [21]. Bursten has argued that for trivalent uranium, increased 5f orbital extension can lead to significant covalent bonding character [22]. Perhaps the most notable examples of this phenomenon are found in the two uranium carbonyl complexes [UCp$'_3$(CO)] (Cp′ = C$_5$H$_4$SiMe$_3$ [23], C$_5$HMe$_4$ [24]), where the frequency of the carbonyl stretching mode is reduced from that in free carbon monoxide due to back bonding from the uranium centre. Hence the uranium centre participates in what might be called traditional Dewar–Chatt–Duncanson bonding with CO.

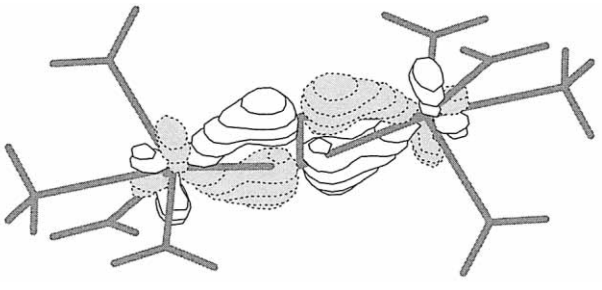

Fig. 2. MOLDEN [32] plot of the α8b$_g$ molecular orbital of a model based on **1** [13]. This corresponds to a π-donor function U → N$_2$.

If such backbonding were taking place in **1** we would normally expect a lengthening of the N–N bond, but this is not observed. Hence, in our original rationalisation of the stability and structure of **1** we suggested [5] that the complex contains what are essentially N$_2$ → U σ-bonds and that [U(NN$'_3$)] is merely acting as an extremely potent Lewis acid. Subsequent results arising from exceptionally high Lewis acidity of a similar cerium system supported this idea [9]. The preference for side-on over the more commonly observed end-on [25] coordination was explained on the basis that the dinitrogen π$_p$ orbital is a better σ-donor than the σ$_p$ to trivalent uranium. However, subsequent quasi-relativistic non-local density tunctional theory calculations on a model system based on **1** showed to our surprise that the only significant U–N$_2$–U interaction is covalent U 5f → N$_2$ π$_g$ backbonding and that the dative a interaction proposed above is essentially absent [13]. This type of π metal/ligand interaction, depicted in Fig. 2, is unusual among the actinides, though not unprecedented [22]. A similar situation, viz. U → (η^6-arene) δ back-bonding was described recently in an inverted sandwich complex [26].

The bridging mode of coordination of dinitrogen to a d-block metal centre, i.e. M(μ-N$_2$)M is commonly observed because the process of M → N$_2$ back donation from one metal renders it a better base to the second metal. Hence, the fact that **1** is a bimetallic compound argues for the U → N$_2$ backbonding proposal arising from our theoretical study [13]. That this backbonding is not accompanied by lengthening of the N–N bond is intriguing, and has been the subject of extensive additional calculations. One such study focused on the geometric and electronic structures of UN$_2$ in spin states ranging from singlet to septet [27]. The primary conclusion from this work was essentially the same as from our earlier study [13], suggesting that metal → N$_2$ backbonding is the dominant interaction in side bound UN$_2$ and that the optimised N–N distance is significantly longer than in free dinitrogen. Extension of this work to U(μ-N$_2$)U in spin multiplicities up to 13 has done nothing to alter this conclusion [28].

Why, then, is the N–N bond in **1** so short? We suggested previously that the strong directionality of the U 5f orbitals (arising from their high nodality) may be the answer, in that lengthening of the N–N bond would reduce the metal 5f/N$_2$ π$_g$ overlap, thus weakening the overall U–N$_2$–U interaction [13]. This explanation seems unlikely in light of the UN$_2$ and U(μ-N$_2$)U calculations described above. A more plausible explana-

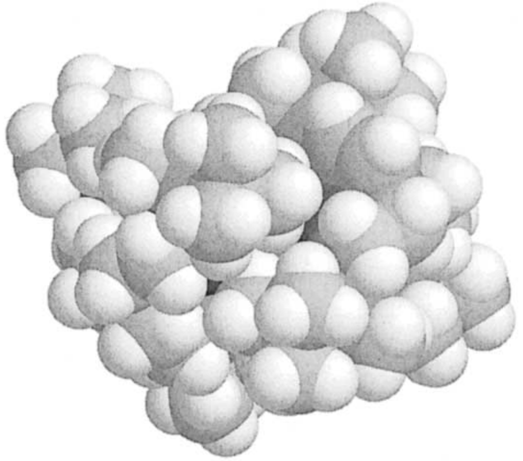

Fig. 3. Space-filling (van der Waals) representation of the molecular structure of **1** showing the interlocking of the $SiMe_2Bu^t$ groups. The minimum U···U non-bonded distance is determined by steric compression between these triamidoamine substituents, not the detail of the $U(\mu\text{-}N_2)U$ interaction.

tion presents itself from steric arguments. The computational N–N lengthening that is the result of π back-bonding is always accompanied by significant $U–N_{(N_2)}$ bond length reduction; up to 0.5 Å in some cases. In the model systems studied there is no steric barrier to this U–N (and, crucially, U–U) shortening. However, in **1** the bulky NN'_3 ligands prevent any shortening of the $U–N(N_2)$ and hence U–U distance. It is apparent from the space-filling model of **1** depicted in Fig. 3 that shortening of the U–U distance is prevented by steric compression between the NN'_3 ligands. We therefore suggest that while there is a strong electronic driving force toward N–N lengthening in **1**, this is opposed by the *steric* constraints of the interlocking NN'_3 ligands.

2.3. Other reactions of [U(NN′₃)] with π-acid ligands

Given the unique way in which the uranium centre of $[U(NN'_3)]$ interacts with dinitrogen we were keen to make similar discoveries for other Dewar-compliant ligands, including H_2, alkynes, CO and isocyanides.

There was no observable reaction between dihydrogen and $[U(NN'_3)]$. The green products isolated from the reaction between $[U(NN'_3)]$ and carbon monoxide, 2-butyne and *tert*-butylisocyanide contained U(IV) centres in each case (as evidenced by their colour and UV spectra), indicating that the incoming ligands had been reduced. Unfortunately, these compounds all resisted strenuous efforts at crystallographic characterisation and gave ambiguous NMR and other data.

3. Conclusion

We have demonstrated extraordinary reactivity of the trivalent complex $[U(NN'_3)]$ in the preparation of the first dinitrogen complex of a 5f element. The fact that Cummins' related tris(anilide) uranium complex [6] does not also independently react with N_2 (vide supra) may be traced to an issue that arose during our investigations into the cerium triamidoamines [9]. Here we noted that a pseudo-trigonal monopyramidal complex such as $[U(NN'_3)]$ does not have to rearrange its ligands in order to accommodate an incoming group, and this greatly enhances the Lewis acidity of the metal centre, and indeed its ability to interact in any way with a weakly bound ligand. In other words the preorganised structure of $[U(NN'_3)]$ plays a significant part in the balance of enthalpy and entropy terms associated with the process of coordination of N_2.

More conventional steric effects play further roles in the make-up of **1**. Firstly the inherent ability of the uranium(III) centres to partake in π-back donation to side-on bound dinitrogen is to an extent thwarted by the bulk of the spectator triamidoamine ligature which prevents closer approach of donor and acceptor. In Dewar terms, the degree of overlap between metal f and ligand π* orbitals is less than optimal, and thus the N–N bond distance is hardly purturbed. Secondly, the dinitrogen ligand in the complex is protected by a tightly interlinked matrix of aliphatic foliage.

As we have previously noted [13], there is no $N_2 \rightarrow U$ dative σ-bond in **1**, the π_u orbitals on dinitrogen being rather too low in energy for the task.

Hence although the dinitrogen complex **1** does not comply well with Dewar's σ-donation/π-back donation bonding model, his timeless work does provide a conceptual framework on which our understanding of this unique molecule is built.

4. Experimental

4.1. General details

All manipulations were carried out under an inert atmosphere of argon using either standard Schlenk techniques or an MBraun dry-box unless otherwise stated. NMR samples were made up in the dry box and the sample tubes were sealed in vacuo or using Young's type concentric stopcocks. Pentane was pre-dried over sodium wire and then distilled over sodium–potassium alloy under an atmosphere of nitrogen and then saturated with argon. Deuterated benzene was dried over molten potassium and distilled trap-to-trap in vacuo. NMR spectra were recorded on a Bruker DMX-300 spectrometer and the spectra referenced internally using residual protio solvent resonances relative to tetramethylsilane ($\delta = 0$ ppm). Infra red spectra were obtained as Nujol mulls in an air-tight holder using a Perkin–Elmer FTIR spectrometer. UV–vis spectra were obtained as pentane solutions in an air-tight quartz cell (path length = 0.1 cm) using a Jasco V-540 spectrometer. El mass spectra were obtained on a VG Autospec mass spectrometer by Dr Ali Abdul-Sada. Elemental Analyses was performed by Mr A. Stones, University College London.

4.2. $[\{U(NN'_3)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$ (**1**)

A stirred solution of $[U(NN'_3)]$ (0.5 g, 0.69 mmol) in pentane (7 cm^3) was exposed to dinitrogen gas at just over 1 atm to give an intense red solution. The solution was filtered and cooled to −20°C to give dark red crystals (0.36 g, 71%).

Anal. Calc. for $C_{48}H_{114}N_{10}Si_6U_2$: C, 39.06; H, 7.78; N, 9.49. Found C, 39.14; H, 7.82; N, 9.62%. ^{1}H-NMR (293 K benzene-d_6) δ 10.8 (s, 12H, CH_2), 7.76 (s, 12H, CH_2), 3.79 (s, 54H, Bu^t), −20.81 (s, 36H, Me_2Si). MS (EI) m/z 723 (100%, $M^+ - UNN'_3N_2$), 685 (15%, $M^+ - UNN'_3N_2 - Bu^t$). IR (Nujol) 1378(s), 1345(s), 1287(w), 1247(s), 1122(s), 1077(s), 1038(m), 1005(m), 957(s), 937(s), 826(s), 736(m), 649(m). UV λ_{max} nm (ε M^{-1} cm^{-1}) 535 (1034), 680 (608), 775 (415), 832 (230), 856 (201). Magnetic susceptibility (Evans method 225–293 K) $\mu_{eff} = 3.22$ BM, $C = 1.30$, $\theta = -116.02$ K.

4.3. Molecular structure of $[\{U(NN'_3)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$ (**1**)

Crystal data for **1**. Dark red air sensitive block 0.24 × 0.20 × 0.12 mm, $C_{48}H_{114}N_{10}Si_6U_2$, $a = 19.549(2)$, $b = 16.2751(14)$, $c = 21.517(2)$ Å, $\beta = 105.611(3)°$, $U = 6593.2(5)$ Å^3, monoclinic, $P2_1/n$, $Z = 4$, total reflections 37 333, independent reflections 14 318, $R_{int} = 0.063$, $\theta_{max} = 28.62$. R_1 $[I > 2\sigma(I)]$, wR_2 and number of parameters were 0.0494, 0.0758 and 625.

A crystal was coated with inert oil and transferred to the cold N_2 gas stream on the diffractometer (Siemens SMART three-circle with CCD area detector). Absorption correction was performed by multi-scan (SADABS) [29]. The structure was solved by direct methods using SHELXS [30] with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined (where appropriate) using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameters $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for methyl groups. The structure was refined on F^2 using SHELXL-96 [31].

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Refcode: PUKPEQ. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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