Evidence for actinide metal to ligand π backbonding. Density functional investigations of the electronic structure of $[\{(NH_2)_3(NH_3)U\}_2(\mu^2\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$

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The electronic structure of $[\{(NH_2)_3(NH_3)U\}_2(\mu^2\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$, a model for the first dinitrogen compound of an actinide, is investigated computationally using quasi-relativistic non-local density functional theory; the only significant U–N_2–U interaction is found to be U→N_2 π backbonding.

The instability of f element complexes with π acid ligands is presumed to arise from the inability of these metals to take part in metal→ligand backbonding. Indeed the bonding in f element compounds is widely regarded as being essentially electrostatic. Nevertheless the physicochemical properties of certain actinide systems cannot be satisfactorily explained without invoking appreciable metal–ligand covalency.[1–4]

We have recently reported our discovery of the first dinitrogen complex of an actinide element, $[\{(NN'_3)U\}_2(\mu^2\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$ $[NN'_3 = N(CH_2CH_2NSiBu^tMe_2)_3]$ **1** (Fig. 1).[5] This compound, synthesised by the exposure of the 'base-free' triamidoamine $[(NN'_3)U]$ to rigorously pure dinitrogen, features an N_2 unit bridging the two uranium centres in a side-on manner. This coordination geometry raises the intriguing and fundamental question of how the N_2 ligand interacts with the metal atoms. The N–N distance [1.109(7) Å] is similar to that found in dinitrogen gas (1.0975 Å), and the magnetic susceptibility and UV–VIS spectrum are very close to those of the parent $[(NN'_3)U]$. These data led us to suggest that **1** contains essentially N_2→U σ bonds, with $[(NN'_3)U]$ acting as an extremely potent Lewis acid. We noted, however, that since the unobserved 1 : 1 intermediate $[(NN'_3)U\text{–}(N_2)]$ is clearly more basic than free dinitrogen, some degree of U→N_2 backbonding may be present.

In order to gain insight into the electronic structure of **1** and hence to evaluate the above suggestions, we have carried out density functional calculations§ on the model complex $[\{(NH_2)_3(NH_3)U\}_2(\mu^2\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$ **2**. Bond lengths and angles were taken from the crystallographic data obtained on **1**, and the molecular structure was idealised to C_{2h} symmetry. The replacement of the triamidoamine ligand by $(NH_2)_3(NH_3)$ is necessary for calculational feasibility and, while such a simplification is not insignificant, we anticipate that the fundamental features of the U–N_2–U interaction will not be greatly affected. Indeed, we have previously used this ligand replacement in other studies.[6]

1 is paramagnetic, with a susceptibility of 3.22 μ_B per uranium atom.[5] It is therefore appropriate to address the electronic structure of **2** using the spin unrestricted approach, in which α and β spin electrons occupying a molecular orbital (MO) of a given number and symmetry are not constrained to have the same spatial wavefunction. The excess α over β spin density is a user-defined parameter within ADF, raising the question of how many unpaired electrons **1** and **2** possess. The spin-only formula is inappropriate for actinide complexes, and thus the magnetic susceptibility of **1** cannot be straightforwardly related to the number of unpaired electrons. Consideration of all the available experimental data suggests that **1** has six unpaired electrons per molecule, *i.e.* that each uranium atom is best regarded as a U^{III} f^3 centre. We have carried out a range of spin unrestricted calculations of **2**, and have found that the most stable electronic arrangement has four unpaired electrons. Imposition of six unpaired electrons produces a non-Aufbau orbital occupation and a markedly less stable structure.¶ We stress, however, that the general features of the electronic structure are very similar in all cases, and it is to these that we now turn.‖

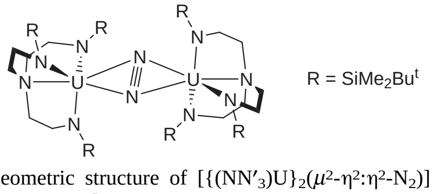

Fig. 1 The geometric structure of $[\{(NN'_3)U\}_2(\mu^2\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$ $[NN'_3 = N(CH_2CH_2NSiBu^tMe_2)_3]$ **1**

A MO energy level diagram for **2** with four unpaired electrons is given in Fig. 2. The orbitals are labelled according to the C_{2h} irreducible representations that they span, together with an α or β designation to indicate the spin of the electron in that orbital. The use of the spin unrestricted approach doubles the number of MOs, and there are 42 such energy levels in the eigenvalue range −8.3 to −2.3 eV. Fortunately the MOs are concentrated in a few groups of similar energy and composition (represented by rectangles on Fig. 2), simplifying the analysis of the valence electronic structure. MOs around the highest occupied orbital are shown on an expanded scale.

The three groups of MOs with energies centred around −8.2, −7.5 and −5.5 eV are largely localised on the NH_2 and NH_3 ligands, with some levels also containing small contributions from the uranium atoms. These orbitals are primarily responsible for binding the NH_2 and NH_3 groups to the metal atoms, as

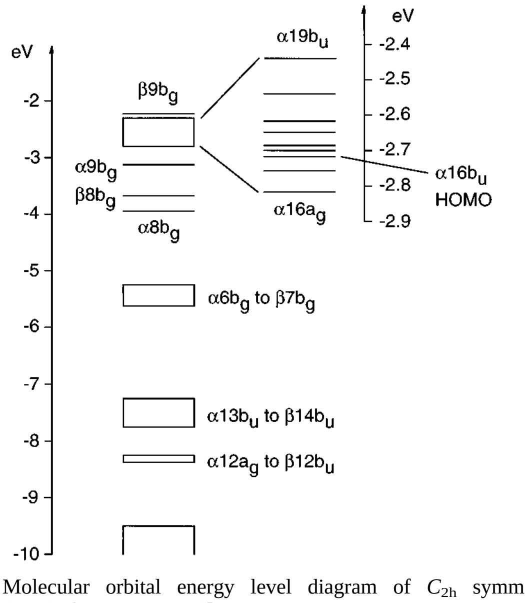

Fig. 2 Molecular orbital energy level diagram of C_{2h} symmetric $[\{(NH_2)_3(NH_3)U\}_2(\mu^2\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$ **2**

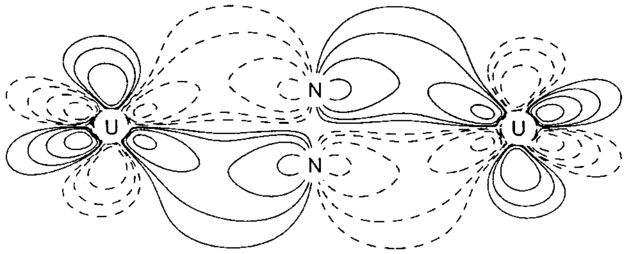

Fig. 3 Contour plot of the α8b$_g$ molecular orbital of [{(NH$_2$)$_3$(NH$_3$)U}$_2$(μ^2-η^2:η^2-N$_2$)] **2**, viewed in the plane defined by the two uranium atoms and the N$_2$ unit. Contour levels are ±0.2, ±0.1, ±0.05 and ±0.025.

well as for some N–H bonding. Given that we are concerned mainly with the U–N$_2$–U interaction, these orbitals will not be discussed further.

The six least stable electrons occupy the α8b$_g$ to α16b$_u$ orbitals. Five of these levels have α spin and one has β spin, and the spatial symmetry of the unpaired electrons is such that the overall molecular electronic state is ^{5}A$_u$. The four orbitals of α spin that have no filled β spin counterpart (α9b$_g$ to α16b$_u$) are predominantly uranium f based ($\geqslant$75% in all cases). The α and β 8b$_g$ orbitals, however, are rather different from this group, in terms of both energy ($>$0.6 eV more stable) and composition. These two levels are mixtures of uranium f and the N–N antibonding π_g orbital of the N$_2$ ligand,** and are U$\rightarrow$N$_2$ π backbonding. A contour plot of the α8b$_g$ orbital is shown in Fig. 3. Analysis of all of the filled MOs of **2** shows that this is the only significant U–N$_2$–U interaction. MOs with contributions from the π_u N–N bonding orbital lie at much more negative eigenvalues (*ca.* -11 to -12 eV) and have negligible uranium character. The Mulliken overlap population between the uranium atoms and the N$_2$ fragment is +0.25 electrons, reinforcing the conclusion of appreciable U–N$_2$–U covalency, and the calculated charge on the nitrogen atoms of the N$_2$ unit (-0.49) indicates a net transfer of electron density from metal to ligand.

Population of the N$_2$ π_g antibonding MO would be expected to produce a lengthening of the N–N bond. That no significant increase is observed experimentally merits further investigation. The strong directionality of f orbitals (arising from their high nodality) suggests one possible explanation. Lengthening the N–N bond would reduce the overlap between the metal f and N$_2$ π_g levels, weakening the U–N$_2$–U bonding interaction. Work is in progress to evaluate this and other hypotheses.††

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Notes and References

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§ Calculations were performed with the Amsterdam Density Functional program suite.[7,8] Quasi-relativistic[9] frozen cores were used for N (1s) and U (5d). Relativistic core potentials were computed using the ADF auxiliary program 'Dirac'. An uncontracted triple-zeta Slater-type orbital valence basis set was employed for all atoms, supplemented with p and d polarisation functions for H (ADF Type V), and d and f polarisation functions for N (ADF Type V). No polarisation functions were included for U (ADF Type IV). The density functional of Vosko *et al.*[10] was employed in conjunction with Becke′s gradient correction[11] to the exchange part of the potential and the correlation correction due to Perdew.[12] Mulliken population analyses were performed.[13] The calculations were performed on IBM RS/6000 and DEC 433au workstations and the EPSRC's 'Columbus/Magellan' computer.

¶ The non-Aufbau, six unpaired electron arrangement is 102 kJ mol^{-1} less stable than that with four unpaired electrons, which has an Aufbau orbital occupancy and which is 68 kJ mol^{-1} more stable than the Aufbau restricted (*i.e.* no unpaired electrons) arrangement.

‖ It should be noted that a full description of the electronic structure of **2** must include the effects of spin–orbit coupling.[14] Under these circumstances the number of unpaired electrons is a meaningless quantity, as the electronic spin and orbital angular momenta cannot be separated. We will address this issue in further studies of triamidoamine–uranium systems.

** *E.g.* the principal contributions to the α8b$_g$ orbital are 24.34% U f$_{z(x^2-y^2)}$, 14.97% U f$_{z^3}$, 6.13% U d$_{yz}$ and 40.23% N$_2$ π_g.

†† Two areas that we will concentrate on are (a) geometry optimisations of **2** (in order to establish if the lack of N–N lengthening is indeed a result of f-orbital/π_g overlap requirements) and (b) replacement of one of the NH$_2$ H atoms by a SiH$_3$ unit in order to model the N(CH$_2$CH$_2$NSiBu^{t}Me$_2$)$_3$ ligand more closely.

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