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Electronic Structure of $[U_2(\mu^2\text{-}N_2)(\eta^5\text{-}C_5Me_5)_2(\eta^8\text{-}C_8H_4(SiPr^i{}_3)_2)_2]$

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Density functional calculations on the model compound $[U_2(\mu^2\text{-}N_2)(\eta^5\text{-}C_5H_5)_2(\eta^8\text{-}C_8H_6)_2]$ support the formulation of the recently characterized dinitrogen complex $[U_2(\mu^2\text{-}N_2)(\eta^5\text{-}C_5Me_5)_2(\eta^8\text{-}C_8H_4(SiPr^i{}_3)_2)_2]$ as containing two U(IV) f^2 centers bridged by a $N_2{}^{2-}$ ligand. The N−N distance found experimentally (1.232 Å) can be modeled only in a geometry optimization by a non-aufbau occupation of the orbitals. Though both N_2 π_g orbitals overlap significantly with U 5f orbitals, only the more stable of the two is occupied in the optimum calculation.

Introduction

The interaction of transition metals with ligands possessing low-lying empty π-acceptor orbitals can be described by two models. One is the well-established concept of π back-donation such as is commonly found for the interaction of d-block metals with CO.[1] The other is oxidation of the metal and reduction of the ligand, normally accompanied by some donation of the transferred electrons back to the metal; this type of interaction is exemplified by the formation from dioxygen of peroxide complexes. Molecular orbital (MO) theory enables these two models to be seen as extremes in a continuum; the metal and ligand have orbitals of appropriate symmetry to overlap and form a metal−ligand bonding MO which is occupied by the electrons in question. If the metal is the major contributor to this MO, the back-donation model is appropriate. If ligand character predominates, a redox model gives a more helpful description. If, as is normally the case, the empty ligand orbital is antibonding in the free ligand, both models give an increase in a ligand internal bond length. The redox model would involve the greater change.

Back-donation commonly involves low-spin metal centers and is favored by d-block transition metals where such electronic configurations are common. For f-block transition metals the f orbitals are less radially extended, they interact only weakly with the ligands, and spin-pairing is energetically unfavorable. Also the high electropositivity of lanthanides and actinides makes the redox model more probable.

The recent synthesis of $[U_2(\mu^2\text{-}N_2)(\eta^5\text{-}C_5Me_5)_2(\eta^8\text{-}C_8H_4(SiPr^i{}_3)_2)_2]$ from $[U(\eta^5\text{-}C_5Me_5)(\eta^8\text{-}C_8H_4(SiPr^i{}_3)_2)]$ conforms to this expectation.[2] The starting U complex is U(III). The bridging N−N distance in the dimer is 1.232(10) Å, consistent with the presence of $N_2{}^{2-}$ and oxidation of the two U centers to U(IV). The dinuclear side-on ($\mu-\eta^2$:η^2) mode of bonding has been observed for group 4 transition metals where N−N distances of 1.43−1.55 Å indicate $N_2{}^{4-}$.[3] Octaethylporphyrin lanthanide complexes (Ln = Pr, Nd) with ($\mu-\eta^2$:η^2-N_2) have N−N distances of 1.25 and 1.23 Å.[4] However, $[Sm(\eta\text{-}C_5Me_5)_2]_2(\mu-\eta^2:\eta^2\text{-}N_2)$ is reported as having an N−N distance of 1.088(12) Å, although other distances and the ^{13}C NMR data indicate that the oxidation state of Sm is 3+.[5] Thus in this case apparent reduction of the N_2 unit does not appear to result in N−N bond lengthening. The other example of ($\mu-\eta^2$:η^2-N_2) bonding for U is the complex $[(N_3N'U)_2(\mu-\eta^2:\eta^2-N_2)]$ ($N_3N' = N(CH_2NSiBu^tMe_2)_3$), where the N−N bond length of 1.109(7) Å is essentially the same as in free dinitrogen.[6] UV/visible spectra and magnetic data suggest in this case that U is in the +3 oxidation state, although the magnetism is also consistent with U(IV). In both cases the binding of N_2 has been attributed to the Lewis acidic nature of the metal center, although in the U case calculations subsequently indicated that back-donation from U 5f orbitals to the π_g orbitals of the N_2 ligand is the only significant metal−N_2 interaction.[7] This conclusion, while unusual in actinide chemistry, is not unprecedented. Experimental[8] and theoretical[9] studies of $[UCp'_3CO]$ ($Cp' = \eta^5\text{-}C_5H_4SiMe_3$) concluded that the CO ligand binds to the U center via a classic Dewar−Chatt−Duncanson mechanism.[1] In this system, the C−O bond is, as expected, longer than in free CO. The surprising lack of bond lengthening in $[(N_3N'U)_2(\mu-\eta^2:\eta^2-N_2)]$ was

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attributed to the steric bulk of the N_3N' ligand preventing close approach of the U to the bridging N_2 and consequent prevention of optimal overlap with the π_g orbital.[10,11]

We have carried out density functional calculations in order to model the electronic structure of the dinitrogen dimer, $[U_2(\mu^2\text{-}N_2)(\eta^5\text{-}C_5Me_5)_2(\eta^8\text{-}C_8H_4(SiPr^i_3)_2)_2]$.

Computational Methods

Density functional calculations were carried out using the Amsterdam Density Functional program suite ADF 2002.02.[12−16] Scalar relativistic corrections were included via the ZORA method. The local density parametrization of Vosko, Wilk, and Nusair[17] was employed, together with the gradient corrections by Becke (exchange)[18] and Perdew (correlation);[19] this is normally described as BP86. The cores of the atoms were frozen up to 1s for C and N and 5d for U, the U 6s and 6p orbitals being included in the valence set. Uncontracted, Slater-type valence functions of triple-ζ quality were employed, with two polarization (valence l+1 and l+2) added to the nonmetal atoms.

For $[U_2(\mu^2\text{-}N_2)(\eta^5\text{-}C_5H_5)_2(\eta^8\text{-}C_8H_6)_2]$ the starting geometry was taken from the crystal structure of $[U_2(\mu^2\text{-}N_2)(\eta^5\text{-}C_5Me_5)_2(\eta^8\text{-}C_8H_4(SiPr^i_3)_2)_2]$ and idealized to C_2 symmetry. The initial geometry optimization was carried out as a spin-restricted calculation with electron density smeared over the frontier orbitals to assist SCF convergence. Subsequent geometry optimizations explored spin states of $S = 0$, 1, and 2 and fixing the configurations to achieve the best agreement with the distances in the U_2N_2 core and the minimum energy.

Results and Discussion

To facilitate the calculation of the title complex, a model compound $[U_2(\mu^2\text{-}N_2)(\eta^5\text{-}C_5H_5)_2(\eta^8\text{-}C_8H_6)_2]$ was chosen in which the ring substituents were replaced by hydrogen atoms.

DFT methods work by identifying a configuration for a molecule. This poses several problems for calculations on open shell actinides. The electronic structure is not normally well described by a single configuration, as spin−orbit, spin−spin, and ligand field effects are all important in obtaining a good description of the ground state. Often SCF convergence to a single configuration with defined spin is difficult to achieve, as there are a large number of orbitals close to the Fermi surface of the molecule. One compensating feature is that the molecular geometry is typically not very sensitive to the exact description of the f electrons.

Our approach was to use as high a symmetry as possible for the model compound, in this case C_2, and carry out a preliminary spin-restricted geometry optimization with the electron density "smeared" over the frontier orbitals in order to assist SCF convergence. In such a calculation the frontier orbitals have fractional occupancy. The resulting orbital energy manifold was then inspected, and further spin-unrestricted geometry optimizations were carried out in a variety of spin states with fixed orbital occupations.

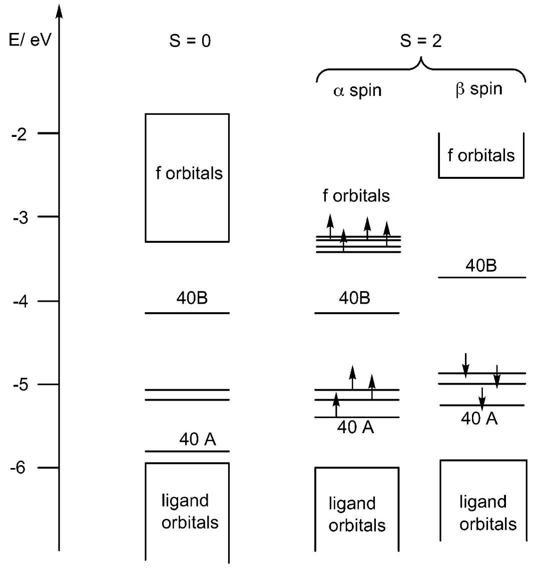
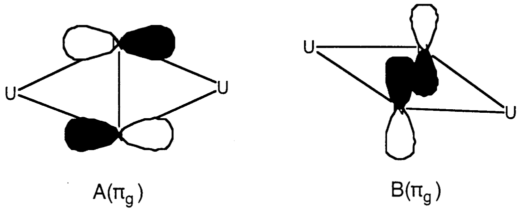


Figure 1. MO scheme for $[U_2(\mu^2\text{-}N_2)(\eta^5\text{-}C_5H_5)_2(\eta^8\text{-}C_8H_6)_2]$. The $S = 0$ level diagram is a spin-restricted calculation with electron density smeared over the upper orbitals. The $S = 2$ calculation is an unrestricted calculation with four unpaired electrons and orbital 40B is empty.

In C_2 symmetry, the π_g orbitals of the bridging dinitrogen ligand transform as A and B in symmetry. The $A(\pi_g)$ orbital points to the U atoms, whereas the $B(\pi_g)$ orbital lies parallel to the $C_2(z)$ axis.



These two orbitals are easily distinguished in the initial calculation (done with $S = 0$) as predominating in MOs 40A and 40B, respectively. The orbital energy ordering is shown in Figure 1. The electron occupancy of 40A was 2.00 and that of 40B was 1.57 in the "smeared" calculation, and the N−N distance optimized to 1.294 Å, rather longer than the 1.232 Å found experimentally.

In subsequent calculations the electronic arrangement that gave the best agreement with the crystal structure was with $S = 2$, orbital 40B left empty, and with four unpaired electrons in f orbitals. With such a configuration the resulting N−N distance was 1.23 Å, in excellent agreement with experiment. It is notable that the $S = 2$, four-unpaired-f-electron arrangement was also found to be the most appropriate in our previous studies of $[\{(NH_2)_3(NH_3)U\}_2(\mu^2\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$.[7]

The energies of the spin−orbitals are shown in Figure 1, and orbital surfaces for filled MO 40A and empty MO 40B are shown in Figure 2. Although the filling is clearly non-aufbau, we consider that this configuration gives the best description of the electronic structure. This situation is not without precedent in actinide calcula-

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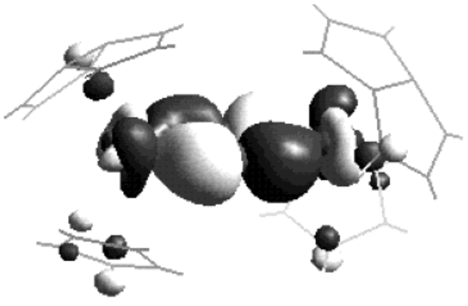
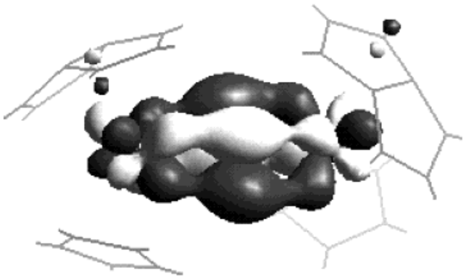


MO 40A



MO 40B

Figure 2. Surfaces for MOs 40A and 40B.

Table 1. Calculated Structural Parameters for $[U_2(\mu^2\text{-}N_2)(\eta^5\text{-}C_5H_5)_2(\eta^8\text{-}C_8H_6)_2]$, I, and $[U(\eta^5\text{-}C_5H_5)(\eta^8\text{-}C_8H_6)]$, II, and Experimental Structural Parameters for $[U_2(\mu^2\text{-}N_2)(\eta^5\text{-}C_5Me_5)_2(\eta^8\text{-}C_8H_4(SiPr^i_3)_2)_2]$, I′, and $[U(\eta^5\text{-}C_5Me_5)(\eta^8\text{-}C_8H_4(SiPr^i_3)_2)]$, II′ (distances in Å angles in deg)[a]

	I	I′	II	II′
N−N	1.232	1.232(10)		
U−N(1)	2.357	2.401(8)		
U−N(2)	2.363	2.423(8)		
U_2N_2 fold	3.5	5		
$U-C_a$ (pent)	2.62−2.65	2.69−2.78	2.61−2.63	2.68−2.73
C_8H_6 fold	29.6	22.5, 26	29.1	26
$U-M_1$	2.394	2.524, 2.505	2.402	2.486(8)
M_1-U-M_2	137.8	136.0, 137.3	169.4	170.1
M_1UM_2 N_1UN_2	60.0	50.5, 59.2		
M_1UM_2 $M_1'U'M_2'$ angle	60.3	69.6		

[a] M_1 is the centroid of cyclopentadienyl ring, and M_2 the midpoint of pentalene bridgehead carbons.

tions[20] and has also been noted in calculations on vanadium porphyrin and phthalocyanine complexes where the ligands have low-lying empty orbitals.[21]

Structural Results. Comparison of the model optimized structure with the experimental observations is given in Table 1. Not only is the N−N distance well reproduced but the U−N distances and the small fold of the U_2N_2 core are in very good agreement. All U−C distances in the model are slightly shorter and the pentalene fold angle is greater than those found experimentally, lending weight to the suggestion that these are controlled to a certain extent by steric interactions. However the discrepancy is not sufficiently great as to invalidate the model.

Also given in Table 1 are distances and angles for $[U(\eta^5\text{-}C_5H_5)(\eta^8\text{-}C_8H_6)]$, optimized with $S = 3/2$, and experimental values for $[U(\eta^5\text{-}C_5Me_5)(\eta^8\text{-}C_8H_4(SiPr^i_3)_2)]$. Again the U−C distances are computed slightly shorter and the fold angle greater than the experimental values. Of particular interest is the fact that there is little variation between the calculated U−C distances in the two model compounds. Thus the formal oxidation of U from III to IV in binding N_2 has little effect on the ligand−metal distances. This was found experimentally to be the case and attributed to the steric bulk of the ligands. The models lack substituents so the invariance of the metal−ligand distances is probably electronic rather than steric.

Fragment Analysis. A fragment analysis was carried out to investigate the interaction of the N_2 unit with the $U(\eta^5\text{-}C_5H_5)(\eta^8\text{-}C_8H_6)$ fragments. The fragments chosen had the geometry found for the optimized structure of the molecule. Thus the N−N distance was lengthened to 1.232 Å from 1.09 Å, the optimized distance in N_2, and the $U(\eta^5\text{-}C_5H_5)(\eta^8\text{-}C_8H_6)$ fragments were bent to an angle of 138°. The results are summarized in Table 2. The principal A symmetry interaction between the fragments is with fragment orbital (FO) 45A, shown in Figure 3. FO 45A is 67% U 5f and 10% U 6d in character. It has a high overlap (0.224) with the A symmetry N_2 π_g orbital. FO 44A (85% 5f) also overlaps but to a lesser extent and lower FOs 37A and 35A also contribute to 40A, as a result of reorganization in the fragment. The directionality of 45A is responsible for the orientation of the bridging N_2 group and also the 60° angle between the M1UM2 planes on the two $[U(\eta^5\text{-}C_5H_5)(\eta^8\text{-}C_8H_6)]$ fragments. It is interesting that the bonding appears to be dominated by the relatively contracted 5f orbitals, rather than by the more diffuse but higher energy 6d set.

The high overlap leads to an MO energy for 40A of −5.42 eV. For MO 40B the overlap between FO 39B (Figure 3) and the B symmetry N_2 π_g MO is 0.11; thus 40B is less stabilized, lying at −4.02 eV.

The almost equal weighting of N and U character in 40A indicates that the bonding is poised between the back-donation and the oxidation model.

In our previous studies of $[\{(NH_2)_3(NH_3)U\}_2(\mu^2-\eta^2{:}\eta^2\text{-}N_2)]$, we found that an *aufbau* occupation was most appropriate. In terms of the orbitals shown in Figure 1, our previous studies placed the 40A level just below the 5f manifold; the equivalent of the 40B MO lay above the 5f electrons. The increased N−N distance in the present calculations may well lead to better U 5f/N π_g overlap, stabilizing the resulting 40A bonding MO and bringing the 40B below the 5f manifold. This obviously raises a question: if we are correct that the *non-aufbau* occupation is a good representation of the electronic structure of the present molecule, why is the calculation compatible with an apparently excited electronic configuration? The method used may well not assess accurately the relative energies of the f and ligand orbitals. More stable f orbitals and less 5f ligand overlap could change the ordering in the orbital manifold in the desired direction. A proper description of the f electrons on the two U centers, including spin−orbit coupling, is likely to lead to a stabilization of the f electrons. The present approach produces an f manifold that is in some way averaged over the atomic $5f_{5/2}$ and $5f_{7/2}$ energies. Spin−orbit coupling will allow the f electrons to settle

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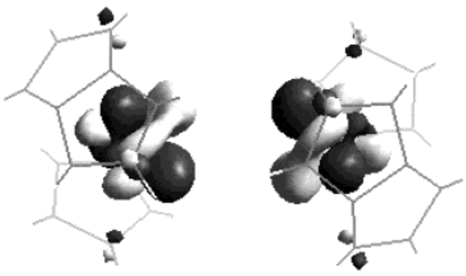
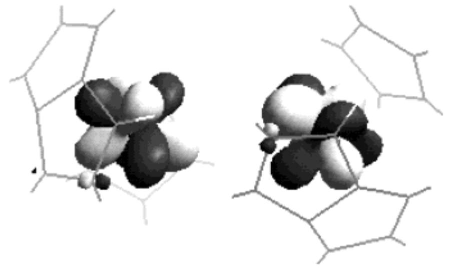
Table 2. Energies (eV) and Compositions of MOs 40A and 40B of $U_2(\mu^2\text{-}N_2)(\eta^5\text{-}C_5H_5)_2(\eta^8\text{-}C_8H_6)_2$[a]

MO	energy	fragment orbital (FO)		energy of FO	% FO in MO	% U 5f in FO	% U 6d in FO	overlap with π_g
40A	−5.42	π_g (A)	N_2	−3.53	47			
		45A	U′	−2.26	16	67	10	0.224
		44A	U′	−2.78	8	85	2	0.071
		37A	U′	−5.20	8			−0.023
		35A	U′	−6.31	8			−0.027
40B	−4.02	π_g (B)	N_2	−3.53	42			
		39B	U′	−2.99	49	85		0.110

[a] The fragments used were $[U(\eta^5\text{-}C_5H_5)(\eta^8\text{-}C_8H_6)]_2$ (denoted U′ in the table) and N_2. The fragments have the geometry found for the optimized structure of the whole molecule.



FO 45A



FO 39B

Figure 3. Surfaces for fragment orbitals 45A, 44A, and 39B.

in the lower energy *j* component. For the free ion U(IV), the $^3H_4$ ground state has a stabilization of 3ζ and ζ for U is approximately 0.25 eV, so a stabilization of 0.75 eV for each U is plausible.

Conclusions

Our calculations strongly suggest that the title compound, $[U_2(\mu^2\text{-}N_2)(\eta^5\text{-}C_5Me_5)_2(\eta^8\text{-}C_8H_4(SiPr^i{}_3)_2)_2]$ is best described as a $N_2{}^{2-}$ complex. Studies on a model for $[U_2(\mu^2\text{-}N_2)(\eta^5\text{-}C_5Me_5)_2(\eta^8\text{-}C_8H_4(SiPr^i{}_3)_2)_2]$ indicate that two electrons occupy an orbital, 40A, built from one component of the N_2 π_g orbitals, U 5f and U 6d orbitals. Each U is best described as having two electrons localized in 5f orbitals, and thus the U configuration is consistent with U(IV). Geometry optimizations with this configuration produce very good agreement with experimental distances. However the orbital occupation that achieves this is *non-aufbau*. Orbital 40 B, which also has N_2 π_g and U 5f character, lies below the 5f orbitals in the energy manifold but has to be empty to reproduce the experimental N−N distance.

We believe, however, that the *non-aufbau* electronic occupation *is* a good representation of the title complex. The calculations may well overestimate metal−ligand overlap. By ignoring configuration interactions and neglecting spin−orbit coupling, they almost certainly underestimate the f electron stability. These conclusions emphasize that calculations such as these must be used with caution as a predictive tool for actinide complexes.

Both the present calculations and our previous work on $[\{(NH_2)_3(NH_3)U\}_2(\mu^2\text{−}\eta^2\text{:}\eta^2\text{-}N_2)]$ indicate that both complexes contain two U(IV) $5f^2$ centers, with substantial covalent interaction between the U 5f atomic orbitals and one component of the N_2 π_g orbitals. This interaction may be characterized as reduction of the N_2 to $N_2{}^{2-}$, and the present calculations concur with experiment in finding an N−N distance appreciably longer than in free N_2. The origin of the short N−N distance in $[(N_3N'U)_2(\mu\text{−}\eta^2\text{:}\eta^2\text{−}N_2)]$ is still not unambiguously resolved. The Raman spectra of these μ^2-N_2 species have not as yet been determined, but would provide valuable confirmation or otherwise of the N−N bond order.

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