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A Molecular Orbital Study of Bonding and Ionization Energies in Pentavalent Uranium Imide/Amide Complexes

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Discrete variational local density functional (Xα) calculations on the model complexes $[(RN)U(NR_2)_3]$ (R = H (**1**), SiH_3 (**2**)) have been performed in order to investigate the electronic structure of uranium amido/imido complexes. Special emphasis is placed on the energy ordering of the highest lying levels formed by U 5f orbitals and by out-of-plane N $2p_\pi$ orbitals. Orbital relaxations are also estimated by studying the fragments NR and NR_2 with R = H and R = $SiMe_3$ in order to allow a comparison of the model compounds **1** and **2** with the measured photoelectron spectrum of the complex $\{(Me_3SiN)U[N(SiMe_3)_2]_3\}$. The ionization energies corresponding to the N $2p_\pi$ MOs are calculated in the order N $2p_\pi$ (amido) < N $2p_\pi$ (imido). The calculated level ordering is rationalized by comparing the order of the two types of U-N bonds and the charge distributions of the corresponding ligands. Taking the calculated ordering as well as the character of the molecular orbitals into account, a new assignment of the observed photoelectron spectra is given based on a comparison of He I and He II spectra.

Introduction

This work was carried out in order to investigate the bonding in complexes containing multiple bonds between uranium and the first-row elements.[1-5] Uranium-carbon multiple bonds have been described as primarily ionic on the basis of the U-C bond lengths, although there is mention of considerable π overlap between uranium and carbon in at least one complex.[6] Uranium imido complexes show both bent[3,4] and linear[7,8] U-N-R geometry, and it is not clear whether this is the result of simple crystal packing forces, as is claimed to be the case for linear and bent imido groups in $[OsO_2(NCMe_3)_2]$,[9] or whether it has an electronic origin, as in the case of main group imide complexes such as $R_3P{=}NR'$.[10] In a recent photoelectron study of a number of uranium(V) imido complexes, uranium 5f and nitrogen $2p_\pi$ ionization potentials were measured, and shifts in the values between different compounds were interpreted in terms of changes in the bonding in the compounds.[11] It was the purpose of the present study to calculate the electronic structure of such complexes to provide further information about the nature of the bonding in them and to check the assignments of peaks in the photoelectron spectra.

Discrete variational (DV) local density functional (LDF) calculations were carried out on the complexes $[(HN)U(NH_2)_3]$ (**1**) and $\{(H_3SiN)U[N(SiH_3)_2]_3\}$ (**2**), which model the known complex $\{(Me_3SiN)U[N(SiMe_3)_2]_3\}$ (**3**). Both relativistic and nonrelativistic calculations were carried out. In previous LDF (Xα) studies of uranium complexes, it was shown that a relativistic treatment is necessary for a proper description of the bonding of uranium compounds.[12-14] Recent applications to tetrahedral uranium complexes[14-16] show that the DV-LDF (Xα) method provides a valuable tool for the interpretation of photoelectron spectra of such compounds.

Method of Calculation

The X-ray crystal structure of **3** shows that this compound has overall C_3 symmetry, with a linear U-N-Si group.[7,8] The molecular geometry of the model complex **2** derived therefrom and atom-numbering system are shown in Figure 1. The symmetry of the complex was raised from C_3 to C_{3v} by placing the Si-N-Si planes vertically and by orienting the hydrogens of the SiH_3 groups appropriately. This has the advantage that one of the symmetry-adapted combinations of the out-of-plane ("π") 2p orbitals of the amide N atoms has symmetry a_2 which is different from that of any of the symmetry combinations of the in-plane orbitals, and so the resulting "π" type orbital in the complex can be readily identified on the basis of symmetry alone. The U-N bond lengths and the N-U-N and U-N-Si angles are taken from a recent, more accurately determined crystal structure of $\{(Me_3SiN)U[N(SiMe_3)_2]_3\}$,[8] in which the amide U-N bond length (2.247 Å) was found to be significantly less than that in the previously published structure (2.295 Å).[7] The Si-H bond was taken as in SiH_4 and tetrahedral angles at Si[17] were used. The relativistic DV-LDF calculations on **2** are quite time-consuming. Therefore, a more complete DV-LDF investigation was carried out on the model compound **1**. Its geometry was derived from that of **2** (see Figure 1) by assuming the N-H bond lengths to be the same in the imide and the amide ligand (1.012 Å[17,18]) and by using trigonal geometry for the amide U-N-H angles (120°).

Calculations were also carried out on the molecular fragments NH, $NSiH_3$, NH_2, and $N(SiH_3)_2$. For NH and NH_2, the geometries were the same as those in the parent uranium complex **1**. For $NSiH_3$ and $N(SiH_3)_2$, the geometries of the NSi parts were the same as those in the parent complex **2**, but with an Si-N-Si angle of 120°.

The molecular orbital calculations were carried out using the DV-LDF (Xα) method,[19] a self-consistent LCAO-MO method within the

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Table I. Orbital Energies ϵ (eV) and Orbital Compositions (%) for the N $2p_\pi$ and U 5f orbitals of $[(HN)U(NH_2)_3]$

nonrelativistic					relativistic				
orbital	$-\epsilon$	composition			orbital	$-\epsilon$	composition		
4e	8.95	$N_i{}^a$	2p	80.3	$9e_1$	8.89	N_i	2p	81.5
		$N_a{}^b$	2p	1.3			N_a	2p	3.7
		U	5f	17.4			U	5f	11.2
		U	6d	0.8			U	6d	3.0
					$4e_2$	8.84	N_i	2p	74.2
							N_a	2p	12.3
							U	5f	9.6
							U	6d	3.3
5e	8.08	N_i	2p	0.2	$5e_2$	8.79	N_i	2p	12.1
		N_a	2p	96.3			N_a	2p	85.2
		U	5f	2.6			U	5f	1.2
		U	6d	0.7			U	6d	1.0
					$10e_1$	8.77	N_i	2p	3.3
							N_a	2p	94.9
							U	5f	0.6
							U	6d	1.1
$1a_2$	8.03	N_a	2p	77.9	$11e_1$	8.50	N_a	2p	91.5
		U	5f	22.1			U	5f	8.5
$6e^c$	6.34	N_i	2p	0.2	$6e_2{}^c$	5.65	N_i	2p	4.0
		N_a	2p	4.5			N_a	2p	2.0
		U	5f	94.6			U	5f	91.6
		U	6d	0.2			U	6d	1.7

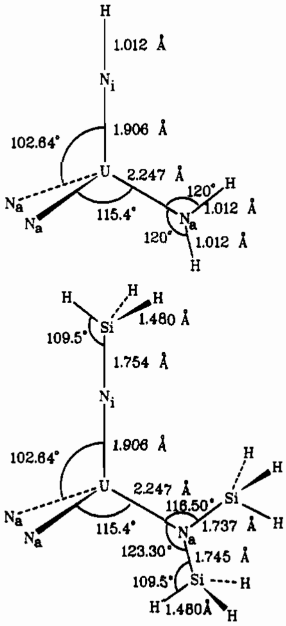
[a] Imide group. [b] Amide group. [c] HOMO, occupied by one electron.

Table II. Orbital Energies ϵ and Ionization Energies I (eV) for the N $2p_\pi$ and U 5f Orbitals of $[(HN)U(NH_2)_3]$ and $\{(H_3SiN)U[N(SiH_3)_2]_3\}$ Compared to Assigned Ionization Energies I for $\{(Me_3SiN)U[N(SiMe_3)_2]_3\}$ from Photoelectron Spectroscopy

orbital type		$[(HN)U(NH_2)_3]$						$\{(H_3SiN)U[N(SiH_3)_2]_3\}$				exptl assign for I	
		nonrelativistic			relativistic			nonrelativistic			relativistic[a]		
		no.	$-\epsilon$	I	no.	$-\epsilon$	I	no.	$-\epsilon$	I	I	new[b]	old[c]
$N_i{}^d$	$2p_\pi$	4e	8.95	12.34	$9e_1$	8.89	12.87	11e	7.70	9.84	10.37	9.5	8.14
					$4e_2$	8.84	12.82						
$N_a{}^e$	$2p_\pi$	5e	8.08	10.79	$5e_2$	8.79	11.40	12e	6.77	8.73	9.33	8.74	8.74
					$10e_1$	8.77	11.39						
$N_a{}^e$	$2p_\pi$	$1a_2$	8.03	10.75	$11e_1$	8.50	11.20	$3a_2$	6.76	8.76	9.21	8.14	8.74
U	5f	6e	6.34	9.49	$6e_2$	5.65	9.19	13e	5.19	7.58	7.28	6.88	6.88

[a] Relativistic value estimated by adding the (averaged) "relativistic" shift calculated for $[(HN)U(NH_2)_3]$ to the nonrelativistic transition-state value I. [b] From experimental photoelectron spectrum for $\{(Me_3SiN)U[N(SiMe_3)_2]_3\}$;[11] suggested new assignments (see also Figure 3). [c] Previous assignments.[11] [d] Imide group. [e] Amide group.

framework of density functional theory.[20-22] The method was applied in a nonrelativistic as well as a relativistic version, solving a one-electron Dirac-type equation in the latter case. Symmetrized molecular orbitals were formed from atomic orbitals, and the atomic configurations for the atoms in the molecule (self-consistent within the framework of a Mulliken population analysis) were determined numerically.[15,19] A double-group formalism was used in the relativistic case.[23] The DV-LDF method takes all electrons into account, but only the valence electrons were included in the self-consistent process (5f, 6d, 7s, and 7p orbitals for U; 2s and 2p for N; 3s and 3p for Si; and 1s for H). The core cutoffs were taken at 3.052, 0.550, and 2.061 au for U, N, and Si, respectively. During the atomic calculations determining the radial basis functions, a spherical potential well was superimposed. The depth of the well was taken constant at −2.0 au up to a radial distance of 4 au; from this value it increased linearly to zero for radial distances between 4 and 6 au. The program used a Fermi distribution of sampling points about each atom for the numerical calculations.[19b] The parameter β in the Fermi distribution was set equal to 1.0, and the Fermi radius to 2.0 au for all atoms. A total number of 24.000 points was used, and their distribution at each atom was adjusted so that their numbers were in the ratio of approximately 1.0:0.2:0.1:0.02 for U, Si, N, and H respectively. However, test calculations showed that the density of points used was sufficiently large that the results were relatively insensitive to changes in these ratios. The iterative SCF procedure was ended when the maximum relative change in potential was less than 10^{-4}.



(1)

(2)

Figure 1. Molecular geometries of the model complexes $[(HN)U(NH_2)_3]$ (**1**) and $\{(H_3SiN)U[N(SiH_3)_2]_3\}$ (**2**).

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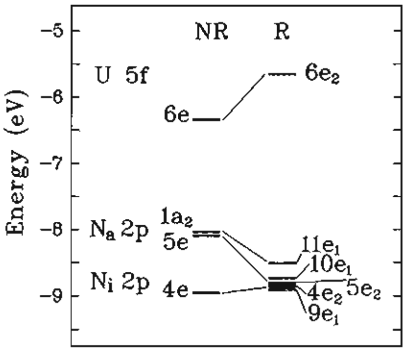

Figure 2. Energies of the four highest lying occupied nonrelativistic (NR) and the corresponding six relativistic (R) orbitals of $[(HN)U(NH_2)_3]$.

Results and Discussion

The orbital energies and orbital compositions for the highest occupied orbitals (which involve mainly the N $2p_\pi$ and the U 5f orbitals) from the nonrelativistic and relativistic calculations on $[(HN)U(NH_2)_3]$ (**1**) are given in Table I, and the orbital energies for both calculations are shown schematically in Figure 2. The order of the orbital energies is U(5f) > $N_a(2p_\pi)$ > $N_i(2p_\pi)$ (N_i = imide nitrogen; N_a = amide nitrogen) for the nonrelativistic calculations. In the relativistic case, however, the $N_i(2p_\pi)$ and $N_a(2p_\pi)$ levels are of almost equal energy, since the amide and imide levels move in opposite directions in going from the nonrelativistic to the relativistic calculation (Figure 2). The ionization energies were calculated by the transition state method,[20] and the results are given in Table II. The relaxation shift of the orbital energies in the transition state is almost uniform (about 2.7 to 3.4 eV) for the nonrelativistic calculations, leading to the same order of the ionization energies as that of the negative of the ground-state orbital energies. For the relativistic calculations, the relaxation shift for the $N_i(2p_\pi)$ level (ca. 4.0 eV) is considerably larger than that for the $N_a(2p_\pi)$ level (ca. 2.6 eV), so that the $N_i(2p_\pi)$ level has the largest ionization potential, despite the fact that the $N_i(2p_\pi)$ and $N_a(2p_\pi)$ orbital energies are similar. Thus, while in all cases the lowest ionization energy is that for U(5f), in agreement with results from photoelectron spectroscopy (PES)[11] of $\{(Me_3SiN)U[N(SiMe_3)_2]_3\}$, the order of the amide $N(2p_\pi)$ and imide $N(2p_\pi)$ is the reverse of that assigned in the PES study.

It should be noted that the calculated ionization energies are much higher than the PES transition energies. This had to be expected when the Me_3Si groups in the parent complex **3** are replaced by H atoms in the model complex **1**. A complete calculation on the parent complex is impossible at this stage, and even the next step of replacing the Me_3Si groups by SiH_3 groups in model **2** is very expensive. Therefore, the calculations on $\{(H_3Si)NU[N(SiH_3)_2]_3\}$ (**2**) had to be restricted to the nonrelativistic case. The results are also shown in Table II together with estimated values for the relativistic transition state energies. The later were obtained by adding the "relativistic" level shift calculated for **1** to the nonrelativistic transition-state energies. The replacement of H by SiH_3 has two effects: a shift in the energies of the N $2p_\pi$ orbitals due to the "electron pushing" by the silyl ligands and a change in the degree of relaxation on ionization of an electron out of these orbitals due to the increased delocalization of the molecular orbitals. The ground-state level shift induced by the silyl ligands is uniformly upward, ranging from 1.15 (U 5f) to 1.31 eV (N_a $2p_\pi$ 5e). The difference in the ionization energies between **1** and **2** increases monotonically with the ionization energy, ranging from 1.91 (U 5f) to 2.50 eV (N_i $2p_\pi$ 4e). The transition-state relaxation shifts are reduced in **2** by about a factor of 0.7 compared to the values obtained for **1**.

Given the calculated ordering $N_a(2p_\pi)$ > $N_i(2p_\pi)$ of the highest lying MOs in both model complexes **1** and **2**, the assignment of the photoelectron spectrum of $\{(Me_3SiN)U[N(SiMe_3)_2]_3\}$ (**3**), suggested previously,[11] has to be reconsidered (cf. Table II). To assist in this task, the He I and He II PE spectra of **3** have been redrawn from ref 11 and superimposed one-to-one as given by the experimentalists (see Figure 3). The two major experimental facts that one has to account for in the assignment are the energy positions and the relative intensities of features in the observed He I and He II PES.[11] In a simplified form, one may state that the higher the admixture of metal 5f and 6d character, the greater the relative intensity of the He II spectrum.[15,24] The pertinent calculational results are the absolute values and the ordering of the ionization energies and the composition of the ground state molecular orbitals. Due to the approximate nature of the model calculations, the first of these three aspects of the theoretical results is probably the least reliable one, the order being possibly uncertain for MOs close in energy.

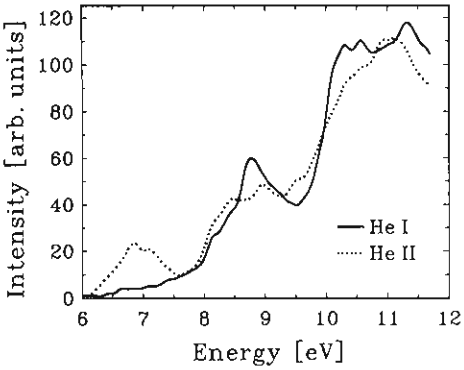

Figure 3. Photoelectron spectra of $\{(Me_3SiN)U[N(SiMe_3)_2]_3\}$. The He I and He II spectra of ref 11 have been redrawn and superimposed.

In broadest terms, the comparison of intensities indicates the following (see Figure 3): (1) one or two bands near 7.0 eV with very great high angular momentum contribution (i.e. U 5f and/or 6d), (2) two components near 8.2 eV with some noticeable fraction of high angular momentum contributions, (3) an important feature near 8.7 eV with relatively little contribution from atomic orbitals of high angular momentum ($l = 2$ and 3), and finally (4) another feature near 9.5 eV that has significant high angular momentum components. Looking at the ground-state results in Table I, one is therefore led to assign band 1 to the 6e ionization potential (IP), band 2 to the $1a_2$ IP, band 3 to the 5e IP, and band 4 to the 4e IP (see Table II). This proposed assignment also agrees with the order of the ionization energies calculated for the model complex $[(HN)U(NH_2)_3]$ (**1**) and for the relativistic estimate of $\{(H_3Si)NU[N(SiH_3)_2]_3\}$ (**2**).

To corroborate this analysis based on the transition-state relaxation shifts of models **1** and **2**, calculations on the ligand fragments NH, $NSiH_3$, NH_2, and $N(SiH_3)_2$ were also performed. The orbital energies and orbital compositions for the fragments are given in Table III. In each case, the HOMO is the one which is identified as "N $2p_\pi$". In the cases of NH and NH_2, the HOMOs are entirely the N $2p_\pi$ orbitals and are nonbonding. In the cases of $NSiH_3$ and $N(SiH_3)_2$, the HOMOs are mainly N $2p_\pi$ but have a significant Si 3d and H 1s component. This has the effect of raising the energy of the HOMO by 0.7 eV in the case of $NSiH_3$ and by 0.9 eV in the case of $N(SiH_3)_2$. This is similar to, although somewhat smaller than, the calculated differences between **1** and **2**. It should also be noted, however, that the N $2p_\pi$ orbital energies for the imide fragments (NH and $NSiH_3$) are higher than those of the amide fragments (NH_2 and $N(SiH_3)_2$), and this order is in agreement with the order originally proposed in the assignment of the PES transitions in the parent complex **3**.[11] However, as discussed above, this order becomes reversed in the calculation on $[(HN)U(NH_2)_3]$, and this must be the result of a difference in the mode of bonding of the NH and NH_2 groups to the uranium atom. This will be discussed in more detail below.

The results of the transition-state calculations for excitation of the N $2p_\pi$ electrons in the NH, $NSiH_3$, NH_2, and $N(SiH_3)_2$ fragments are given in Table IV. These show that the replacement

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Table III. Orbital Energies ε (eV) and Orbital Compositions (%) for NR and NR_2 Fragments for R = H and R = SiH_3

			composition					
			N		Si			H
species	orbital	−ε	2s	2p	3s	3p	3d	1s
NH	1σ	21.53	64.1	7.4				28.5
	2σ	9.09	22.8	68.6				8.6
	1π	6.63		100.0				
$NSiH_3$	$1a_1$	19.38	65.6	4.7	14.5	7.6	4.3	3.2
	$2a_1$	14.02	9.3	1.0	39.1	10.8	2.7	37.1
	1e	10.16		4.3		39.5	3.3	52.9
	$3a_1$	7.48	11.1	70.0	0.9	13.2	0.1	4.7
	2e	5.94		84.2		0.3	9.4	6.1
NH_2	$1a_1$	25.23	53.1	12.9				34.1
	$1b_2$	10.65		66.3				33.7
	$2a_1$	9.26	32.6	63.0				4.5
	$1b_1$	7.37		100.0				
$N(SiH_3)_2$	$1a_1$	21.30	62.3	4.5	13.2	10.5	7.0	2.6
	$1b_2$	14.89		15.9	51.2	0.9		32.5
	$2a_1$	13.84	5.0	0.2	36.9	14.0	3.5	40.4
	$1b_1$	10.54		11.0		37.7	3.2	48.2
	$3a_1$	10.21	0.6	9.6	0.7	42.1	0.8	46.1
	$2b_2$	10.19		41.7	0.1	32.6	1.9	23.7
	$1a_2$	9.80				37.2	5.3	57.5
	$3b_2$	9.19		14.5		33.1	5.3	47.1
	$4a_1$	6.85	5.8	66.1	0.2	2.0	11.7	14.3
	$2b_1$	6.50		75.6			11.6	12.9

Table IV. HOMO (N $2p_\pi$) Orbital Energies ε and Ionization Energies *I* (eV) for NH, NH_2, $NSiH_3$, and $N(SiH_3)_2$

		energy		
species	orbital	−ε	*I*	relaxation
NH	1π	6.63	12.62	5.99
$NSiH_3$	2e	5.94	10.20	4.26
NH_2	$1b_1$	7.37	12.97	5.60
$N(SiH_3)_2$	$2b_1$	6.50	10.01	3.51

Table V. U–N($2p_\pi$) Overlap Populations (per U–N Bond) in $[(HN)U(NH_2)_3]$

orbital type		nonrelativistic		relativistic	
		orbital	pop.	orbital	pop.
N_i[a]	$2p_\pi$	4e	0.216	$9e_1$, $4e_2$	0.269
N_a[b]	$2p_\pi$	5e, $1a_2$	0.037	$5e_2$, $10e_1$, $11e_1$	0.086

[a] Imide group. [b] Amide group.

of H by SiH_3 results in a reduction of the relaxation by a factor of about 0.7, as found previously in the comparison of the nonrelativistic results for the model complexes **1** and **2**. These findings therefore support the suggested new assignment of the photoelectron spectrum given above.

As mentioned above, the amide and imide $2p_\pi$ orbital energies in $[(HN)U(NH_2)_3]$ are the reverse of those of the fragments NH and NH_2, and this suggests that there are substantial differences in the involvement of the N $2p_\pi$ orbitals in these fragments in their bonding to the U atom. One way of examining this is to determine the total π overlap populations for U–N_i and U–N_a for the orbitals which mainly involve the N $2p_\pi$ atomic orbitals. The results are given in Table V and show that the degree of involvement of the imide N $2p_\pi$ orbitals in the covalent bonding to the uranium atom is much greater than that of the amide N $2p_\pi$ orbitals, as one would expect from chemical intuition.

Another way of examining this point is to calculate the degree of charge transfer from the closed-shell $[NH]^{2-}$ and $[NH_2]^-$ fragments to the U atom in the complex. Transfer of no electrons corresponds to pure ionic metal–ligand bonding, whereas transfer of one electron from one of the N $2p_\pi$ orbitals corresponds to a U–N π bond order of unity (a pure covalent π bond). The charge distribution obtained from the population analysis is shown in Figure 4, and the degree of charge transfer from the orbitals of the closed-shell ligands is given in Table VI. These results support the conclusions reached from the overlap populations, namely, that the involvement of the imide N $2p_\pi$ orbitals in the covalent bonding to the uranium atom is considerably larger than that of the amide N $2p_\pi$ orbitals.

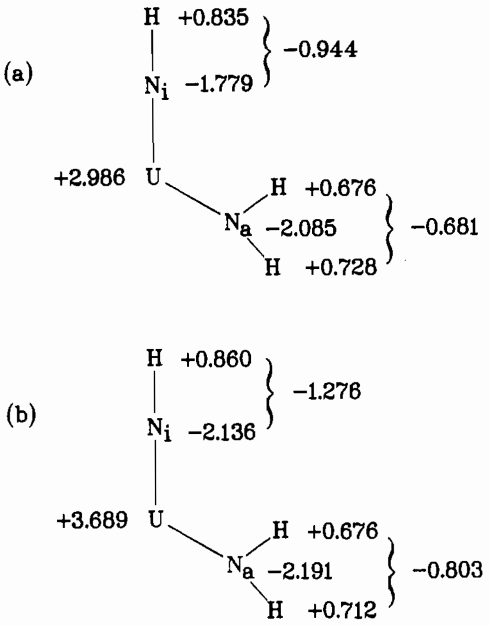

Figure 4. Atomic charges and overall charges on the NH and NH_2 fragments in $[(HN)U(NH_2)_3]$: (a) nonrelativistic calculation; (b) relativistic calculation.

Table VI. Total N($2p_\pi$) Orbital Populations in $[(HN)U(NH_2)_3]$ and Charge Transfer from the Nonbonding $2p_\pi$ Orbitals of the Closed-Shell Ligands $[NH]^{2-}$ and $[NH_2]^-$ to the Uranium Atom

orbital type		nonrelativistic			relativistic		
		orbital	pop.	charge transfer	orbital	pop.	charge transfer
N_i[a]	$2p_\pi$	4e	3.21	0.39	$9e_1$, $4e_2$	3.11	0.44
N_a[b]	$2p_\pi$	5e, $1a_2$	5.41	0.20	$5e_2$, $10e_1$, $11e_1$	5.43	0.19

[a] Imide group. [b] Amide group.

In view of the current research activity in the area of relativistic effects in chemical bonding,[25,26] it is of interest to examine the

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effect of inclusion of relativity on the uranium–nitrogen bonding. This is best seen in the overlap population results in Table V. These show a significant increase in the U–N($2p_\pi$) overlap populations and thus an increase in the U–N π bond strength from the nonrelativistic to the relativistic case. Examination of the forms of the appropriate molecular orbitals (Table I) shows that this is associated with an increase in the contribution of the U 6d orbitals and a decrease in the contribution of the U 5f orbitals to the molecular orbitals. Since the 6d orbitals are more diffuse than the 5f orbitals, this results in an increase in the overlap population and bond strength for the bond concerned. The importance of the role of 6d orbitals in the relativistic description of the bonding in actinide compounds has been pointed out previously.[12] It has also been pointed out previously[13] that nonrelativistic LDF (Xα) calculations overemphasize the covalency contributions of actinide 5f orbitals and underestimate those of 6d orbitals as compared to a relativistic calculation. Inspection of Table I confirms these trends for the present system. However, the 6d contribution to the bonding is small in absolute terms and is also significantly smaller than in the $U(BH_4)_4$ complex.[14]

Conclusions

The calculations carried out to date do not support the assignment of the N $2p_\pi$ transitions in the PE spectrum of $[(Me_3SiN)U(N(SiMe_3)_2)_3]$ (3) given previously.[11] These assignments could be understood if the ligand fragments showed little (or equal) interaction with the uranium atom. However, analysis of the results of the calculations reveals that the imide N $2p_\pi$ orbitals are much more involved in the metal–ligand bonding than are the amide N $2p_\pi$ orbitals, and this effect is sufficient to reverse the orders of the N $2p_\pi$ ionization energies in the complex and lead to a new interpretation of the photoelectron spectrum of complex **3**. Similar bonding effects may be expected for other uranium complexes with multiply-bonded ligands.

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Rearrangements in Square-Planar and Square-Pyramidal Complexes of Palladium(II) and Platinum(II) Containing the Enantiomers of (±)-Methylphenyl(8-quinolyl)arsine and Its Phosphorus Analogue

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Square-planar complexes containing (±)-methylphenyl(8-quinolyl)arsine, As*N, or its phosphorus analogue, P*N, of the type $[M(E^*N)_2](PF_6)_2$ and square-pyramidal complexes of the type $[MCl(E^*N)_2]X$ (where M = Pd(II) or Pt(II), E = As or P, and X = Cl or PF_6) have been prepared in enantiomerically and diastereomerically homogeneous forms and their behavior in solution has been investigated by variable-temperature NMR spectroscopy. The square-planar cations, which have the cis coordination geometry, undergo facile intermolecular ligand redistribution (As > P) for both metals (Pd > Pt); the corresponding square-pyramidal cations show, in addition to the above, even more rapid axial chloro site exchange.

Introduction

Asymmetric bidentates of the type A*B are powerful probes of stability and stereochemistry in metal complexes of the type $[M(A^*B)_n]$ (where $n = 2$ or 3).[1] For the square-planar complexes $[M(A^*B)_2]$ four diastereomers are possible and interconversions between these will be diagnostic of intramolecular rearrangement and intermolecular redistribution.[2] Thus, it is important in designing an A*B bidentate to incorporate within it appropriate substituents for spectroscopic analysis. Accordingly, we synthesized the asymmetric bidentate (±)-methylphenyl(8-quinolyl)arsine, As*N, and the phosphorus congener (±)-methylphenyl(8-quinolyl)phosphine, P*N, and resolved both ligands by the method of metal complexation.[3] With use of the ligands, in optically active and racemic forms, we have now prepared the square-planar complexes $[M(E^*N)_2](PF_6)_2$ (where M = Pd or Pt and E = P or As) and the square-pyramidal derivatives $[MCl(E^*N)_2]X$ (where X = Cl or PF_6) and investigated their behavior in solution by NMR spectroscopic analysis. In earlier work, we had synthesized the SbN ligands dimethyl- and (±)-methylphenyl(8-quinolyl)stibine and isolated the square-planar dichloropalladium(II) and dichloroplatinum(II) derivatives.[4] In other laboratories, the AsN ligands dimethyl- and diphenyl(8-quinolyl)arsine have been synthesized and used to prepare derivatives of palladium(II), platinum(II),[5] ruthenium(II), rhodium(I), and rhodium(III),[6] and the PN ligands bis(dimethylamino)-, diethyl-, dimethyl-, (dimethylamino)methyl-, diphenyl-, and methyl(8-quinolyl)phosphine have been prepared[7] and the coordination compounds of the diphenylphosphino ligand with cobalt(II), copper(II), iron(II), and nickel(II) investigated.[8]

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