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A UV Photoelectron Spectroscopic Investigation of the Bonding in Some Tri-, Tetra-, and Pentacoordinated Dialkylamino Compounds of Chromium, Molybdenum, Niobium, and Tantalum

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Abstract: Helium(I) ultraviolet photoelectron spectra (UV PES) are reported for the compounds $Cr(N\text{-}i\text{-}Pr_2)_3$, $Cr(NEt_2)_4$, $Mo(NMe_2)_4$, $Mo(NEt_2)_4$, $Nb(NMe_2)_5$, and $Ta(NMe_2)_5$. The interpretation of the UV PES of the paramagnetic dialkylamide, $Cr(N\text{-}i\text{-}Pr_2)_3$, was aided by a SCF-X$\alpha$ scattered wave (Xα-SW) calculation on the model compound $Cr(NH_2)_3$. In contrast to previous UV PES work on $Cr[N(SiMe_3)_2]_3$, ionizations are detectable from the metal MOs of $Cr(N\text{-}i\text{-}Pr_2)_3$. The UV PES of the tetracoordinate molybdenum compounds, $Mo(NR_2)_4$, R = Me, Et, are in excellent agreement with X-ray crystallographic data on $Mo(NMe_2)_4$ and exhibit a low-energy ionization (~5.3 eV) which is attributable to electron ejection from the essentially pure Mo 4d$_{x^2-y^2}$ MO of b_1 symmetry. The pentacoordinate compounds, $M(NMe_2)_5$, M = Nb, Ta, exhibit very similar UV PES and therefore appear to be isostructural in the vapor phase.

Introduction

The use of dialkylamido and disilylamido ligands has permitted the isolation of mono- and dinuclear transition metal derivatives with widely varying coordination numbers.[2] Compounds of this type are well suited to investigation by ultraviolet photoelectron spectroscopy (UV PES) because, as shown in previous studies,[3-5] the peaks at lower binding energies corresponding to electron ejection from metal-centered MOs, nitrogen lone pair MOs, and metal–nitrogen σ-bonding MOs fall into distinct regions. The UV PES data can be used, therefore, not only for the delineation of bonding schemes but also for gaining insights into the stereochemistry of metal amides.

The present paper is concerned with the measurement and interpretation of the UV PES of $Cr(N\text{-}i\text{-}Pr_2)_3$, $Cr(NEt_2)_4$, $Mo(NMe_2)_4$, $Mo(NEt_2)_4$, $Nb(NMe_2)_5$, and $Ta(NMe_2)_5$. Our interest in the tricoordinate species, $Cr(N\text{-}i\text{-}Pr_2)_3$, was generated by the fact that in the corresponding silylamide, $Cr[N(SiMe_3)_2]_3$, it was impossible to detect UV PES peaks corresponding to the ionization of metal-localized MOs.[5] The tetracoordinate dialkylamides, $Cr(NEt_2)_4$ and $Mo(NR_2)_4$, R = Me, Et, are the first group 6B amides to be studied by UV PES; particular interest is associated with these compounds because the molybdenum amides are diamagnetic yet $Cr(NEt_2)_4$ is paramagnetic. Finally, the pentacoordinate amides, $M(NMe_2)_5$, M = Nb, Ta, were investigated because of the apparently close energies of the trigonal-bipyramidal and square-pyramidal MN_5 geometries and the possibility of detecting conformational effects in the vapor phase.

A SCF-Xα scattered-wave calculation[6] (hereafter referred to as Xα–SW) has been performed on the model amide $Cr(NH_2)_3$ to facilitate the interpretation of the UV PES data. As is well known, this theoretical approach has the advantage of avoiding the use of Koopmans' theorem[7] by means of the transition-state method.[8]

Experimental Section

Materials. The compounds $Cr(N\text{-}i\text{-}Pr_2)_3$,[9] $Cr(NEt_2)_4$,[10] $Mo(NMe_2)_4$,[11] $Mo(NEt_2)_4$,[11] $Nb(NMe_2)_5$,[12] and $Ta(NMe_2)_5$[13] were prepared and purified as described in the literature.

Spectroscopic Measurements. All UV PES data were recorded on a Perkin-Elmer Model PS-18 photoelectron spectrometer using a He(I) photon source (21.22 eV). The heated inlet probe was used for all samples and temperatures in the range 35–100 °C were necessary to obtain suitable spectra. Each spectrum was calibrated with xenon (12.130 eV) and argon (15.759 eV) used as internal standards. Spectral resolution was maintained between 25 and 50 meV for the argon line. All ionization energies are read as the band maxima, unless otherwise noted, and are the average of at least three different runs.

Computational Procedures. The Xα-SW calculation on $Cr(NH_2)_3$ was made by employing the spin-restricted procedure of Johnson and Slater,[6] setting the occupation numbers of the 6e and $4a_1$ levels at two and one, respectively, in accord with the observed ground-state electronic configuration.[9] The bond distances and angles for $Cr(NH_2)_3$ were based on those observed by X-ray crystallography for $Cr(N\text{-}i\text{-}Pr_2)_3$,[14] except that the N–H bond distance was taken to be 1.01 Å. The atomic sphere radii were chosen on the basis of optimizing the virial ratio, and the outer sphere was set tangential to the hydrogen spheres.[15] Schwartz's exchange parameters, α_{HF}, were used for

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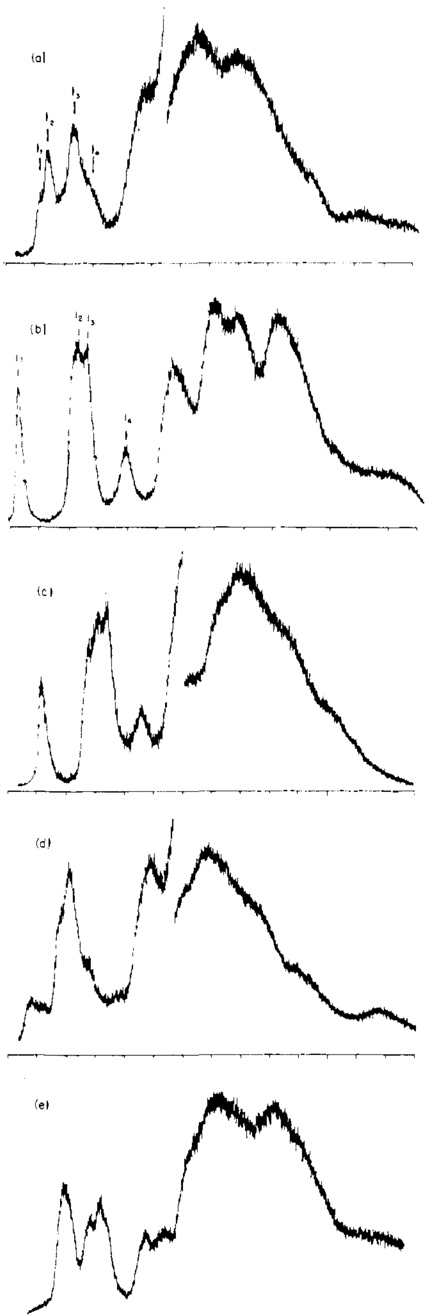

Figure 1. He(I) UV PES of (a) $Cr(N\text{-}i\text{-}Pr_2)_3$; (b) $Mo(NMe_2)_4$; (c) $Mo(NEt_2)_4$; (d) $Cr(NEt_2)_4$; (e) $Ta(NMe_2)_5$.

chromium and nitrogen, while Slater's value for hydrogen was used.[16] α_{outer} was taken equal to α_H, while the intersphere exchange parameter, α_{int}, was calculated to be 0.7490 on the basis of averaging the atomic α values according to the numbers of valence electrons. Spherical harmonics through $l = 2$ were employed for the chromium and outer spheres, while functions through $l = 1$ and 0 were employed for the nitrogen and hydrogen spheres, respectively. All SCF calculations were converged to better than 0.01 eV for each level, maintaining all cores fixed. The first four IEs for $Cr(NH_2)_3$ were computed by the transition-state method.[8]

Results and Discussion

The tricoordinate compounds, $M[N(SiMe_3)_2]_3$, M = Ti, Cr, Fe, and $Cr(N\text{-}i\text{-}Pr_2)_3$ represent examples of the stabilization of low coordination numbers by means of bulky groups. Single-crystal X-ray structures of $Fe[N(SiMe_3)_2]_3$[17] and $Cr(N\text{-}i\text{-}Pr_2)_3$[14] revealed that the MN_3 skeletons are trigonal planar and that ϕ, the dihedral angle between the NX_2 and MN_3 planes, is 49 and 71°, respectively. The other tricoordinate compounds of concern here can be assumed to possess a similar structure. Collectively, ESR data,[14,18] magnetic data,[19] and crystal-field calculations[19] indicate that the ground-state electronic configurations of the silylamides are $Ti[N(SiMe_3)_2]_3$, $^2A_1'$; $Cr[N(SiMe_3)_2]_3$, $^4A_2'$; $Fe[N(SiMe_3)_2]_3$, $^6A_1'$. The dialkylamide, $Cr(N\text{-}i\text{-}Pr_2)_3$, has been shown[9] to have the same ground-state electronic configuration as $Cr[N(SiMe_3)_2]_3$.

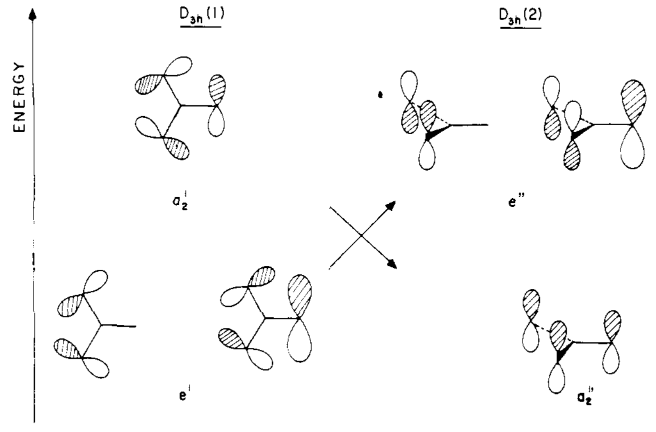

Figure 2. Horizontal ($D_{3h}(1)$, $\phi = 90°$) and vertical ($D_{3h}(2)$, $\phi = 90°$) arrangements of N(2p) AOs in threefold symmetry.

Curiously, despite the presence of unpaired electrons in the above silylamides, no low-energy ionizations attributable to metal-localized orbitals were detectable in the UV PES.[5] The reason which was advanced for this phenomenon is that the metal MOs are stabilized significantly by the more electron-withdrawing $(Me_3Si)_2N$ groups, possibly causing them to be of comparable energies to the nitrogen lone pair MOs. Interestingly, $Cr(N\text{-}i\text{-}Pr_2)_3$ does exhibit peaks at low IE which can be attributed to the ionization of metal-localized MOs (Figure 1a). The detailed assignment of the UV PES of paramagnetic transition-metal systems is, in general, a complicated matter[20,21] because of the large number of ionic states which can be generated upon photoionization (Table I). Arguing qualitatively, and on the basis of intensity considerations, it is reasonable to assign peaks I_1 and I_2 to the production of the $^3A_2$ and ^3E ionic states via electron ejection from the Cr(3d) orbitals of a_2 and e symmetry, respectively (see below). In threefold symmetry the nitrogen "lone pair" MOs span the a_2 and e irreducible representations. However, as is clear from the nodal properties of such MOs (Figure 2), their relative energies are sensitive to the dihedral angle.[22] Obviously, at intermediate values of ϕ, a "crossover" occurs, and at some particular value of ϕ the a_2 and e MOs must be degenerate. Since the dihedral angle between the CrN_3 and NC_2 planes is 71° in $Cr(N\text{-}i\text{-}Pr_2)_3$[14] the symmetry is nearer to $D_{3h}(1)$ than $D_{3h}(2)$. It is on this basis that we assign peaks I_3 and I_4 to the ionization of the a_2 and e nitrogen lone pair MOs, respectively. The lack of resolution of peaks I_3 and I_4 could be due to two factors: (a) the possibility that both triplet and quintet A_2 and E states are observed in this region and (b) Jahn-Teller splitting of the E states. The peak at 9.9 eV obviously represents the onset of ionization of the metal-nitrogen σ-bonding MOs (of symmetry a_1 and e); however, it is difficult to advance specific assignments.

The foregoing, qualitative interpretation of the UV PES of $Cr(N\text{-}i\text{-}Pr_2)_3$ is in good accord with the Xα–SW calculation on the model compound $Cr(NH_2)_3$ (Tables II and III). Thus, the two highest occupied MOs (Table II) are primarily Cr(3d) in composition; the 6e MO is the degenerate $3d_{xz}$, d_{yz} set while the $4a_1$ is primarily $3d_{z^2}$ (if the CrN_3 moiety lies in the *xy* plane). The $3a_2$ and 5e MOs are both mainly nitrogen lone pair;

Table I. Ionic States Resulting from Lower Energy Ionizations of Open-Shell Metal Dialkylamides

ground state	ion configuration	ionic state produced	exptl ionization energies[a]
	$Cr(N\text{-}i\text{-}Pr_2)_3$		
$e^4a_2{}^1a_1{}^1e^2$ [$^4A_2$]	$e^4a_2{}^2a_1{}^1e^1$	^3E	6.53
	$e^4a_2{}^2e^2$	$^3A_2$	6.3
	$e^4a_1{}^1a_1{}^1e^2$	$^3A_1$ $^5A_1$	7.38
	$e^3a_2{}^2a_1{}^1e^2$	^3E ^5E	7.9
			9.9 (M-Nσ)
	$Cr(NEt_2)_4$, $D_{2d}(1)$		
$a_1{}^2b_2{}^2e^4b_1{}^1a_1{}^1$ [$^3B_1$]	$a_1{}^2b_2{}^2e^4b_1{}^1$	$^2B_1$	5.9
	$a_1{}^2b_2{}^2e^4a_1{}^1$	$^2A_1$	6.3
	$a_1{}^2b_2{}^2e^3b_1{}^1a_1{}^1$	^2E ^4E	7.0
	$a_1{}^2b_2{}^1e^4b_1{}^1a_1{}^1$	$^2A_2$ $^4A_2$	7.2
	$a_1{}^1b_2{}^2e^4b_1{}^1a_1{}^1$	$^2B_1$ $^4B_1$	7.9
			10.0 (M-Nσ)
	$Cr(NEt_2)_4$, $D_{2d}(2)$		
$b_1{}^2e^4a_2{}^2a_1{}^1b_1{}^1$ [$^3B_1$]	$b_1{}^2e^4a_2{}^2a_1{}^1$	$^2A_1$	5.9
	$b_1{}^2e^4a_2{}^2b_1{}^1$	$^2B_1$	6.3
	$b_1{}^2e^4a_2{}^1a_1{}^1b_1{}^1$	$^2B_2$ $^4B_2$	7.0
	$b_1{}^2e^3a_2{}^2a_1{}^1b_1{}^1$	^2E ^4E	7.2
	$b_1{}^1e^4a_2{}^2a_1{}^1b_1{}^1$	$^2A_1$ $^4A_1$	7.9

[a] All values in eV.

Table II. Xα-SW "Ground-State" Eignevalues and Charge Densities[a] for $Cr(NH_2)_3$

MO	ϵ^b	Cr				N			H	outer[c]	int[d]
		s +	p +	d =	total	s +	p =	total	s	total	total
7e	−1.00		0.03	0.63	0.66	0.01	0.06	0.07	0.00	0.02	0.11
6e	−3.41		0.00	0.87	0.87	0.00	0.01	0.01	0.00	0.00	0.10
$4a_1$	−3.53	0.07		0.64	0.71	0.00	0.00	0.00	0.00	0.02	0.27
$3a_2$	−4.60		0.00		0.00		0.23	0.23	0.00	0.00	0.31
5e	−5.72		0.04	0.10	0.14	0.00	0.18	0.18	0.00	0.02	0.30
4e	−8.76		0.06	0.26	0.32	0.01	0.18	0.19	0.01	0.02	0.03
$3a_1$	−9.23	0.14		0.13	0.27	0.01	0.19	0.20	0.02	0.00	0.01
$2a_2$	−12.88		0.01		0.01		0.19	0.19	0.07	0.00	0.00
3e	−12.93		0.00	0.02	0.02	0.00	0.19	0.19	0.07	0.01	0.00
2e	−20.69		0.02	0.01	0.03	0.22	0.01	0.23	0.04	0.00	0.04
$2a_1$	−20.81	0.02		0.01	0.03	0.23	0.01	0.24	0.04	0.00	0.01
$1a_2$	−46.28		1.00		1.00		0.00	0.00	0.00	0.00	0.00
1e	−46.38		0.99	0.00	0.99	0.00	0.00	0.00	0.00	0.00	0.01
$1a_1$	−73.51	1.00		0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00

[a] Charge densities for atoms are the percentages of electron densities within the atomic spheres. [b] Eigenvalues in eV. [c] Charge density outside outer sphere. [d] Intersphere charge density inside outer sphere and not accounted for by atomic spheres; dashed line denotes a separation of HOMO and LUMO.

however, while the $3a_2$ is entirely localized on the nitrogens, the 5e has a small, but significant, amount of density on chromium. This orbital is the π-bonding MO of the molecule and the orbital contour of one of the degenerate set is shown (in the *xy* plane) in Figure 3a. Since the nitrogen lone pairs are twisted out of the *xy* plane by only 19°, the best overlap is with the $d_{x^2-y^2}$, d_{xy} set of orbitals on chromium. The wave function in Figure 3a shows nitrogen lone pair overlap with the Cr $3d_{xy}$ orbital. The next two MOs, 4e and $3a_1$, are the σ-bonding orbitals of the molecule. The contour of one of the degenerate 4e wave functions is shown in Figure 3b (*xy* plane), while the contour of the $3a_1$ MO (in the plane along the Cr-N σ bond, perpendicular to the *xy* plane) is illustrated in Figure 3c. The $3d_{z^2}$ contribution to the σ bonding is evidenced from the latter contour. The next four MOs, $2a_2$, 3e, 2e, and $2a_1$, are N-H σ bonding, while the $1a_2$, 1e, and $1a_1$ are entirely Cr 3p and 3s in composition. It appears that the Cr $3d_{x^2-y^2}$, d_{xy} set of e orbitals is involved in π bonding (Figure 3a) as well as σ bonding (Figure 3b) in the molecule.

It is of importance to note that the computed IEs (Table III) for the $4a_1$ and 6e metal-localized MOs are in the reverse order to the ground-state eigenvalues (Table II), i.e., the HOMO (6e) is responsible for the second ionization. The breakdown of Koopmans' theorem in this instance is due to the relatively large relaxation energies which are associated with the photoionization of metal-rich orbitals: the higher the metal d orbital character, the more the MO will relax upon ionization. Thus, the 6e (87% metal) relaxes to a larger extent than the

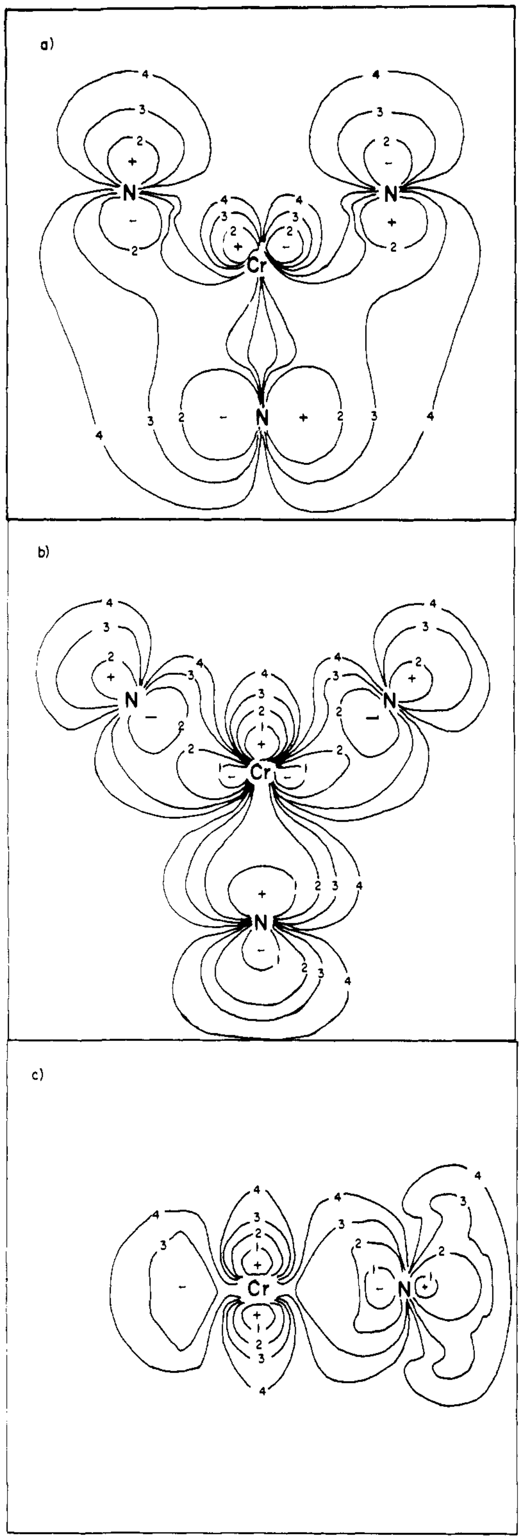

Figure 3. Xα-SW contour plots for the following MOs of Cr(NH$_2$)$_3$: (a) one of the two degenerate 5e wave functions (CrN$_3$ plane); (b) one of the two degenerate 4e wave functions (CrN$_3$ plane); (c) the 3a$_1$ wave function (perpendicular to CrN$_3$ plane, along CrN bond). Contour values follow: 1 = ±0.20; 2 = ±0.10; 3 = ±0.05; 4 = ±0.02.

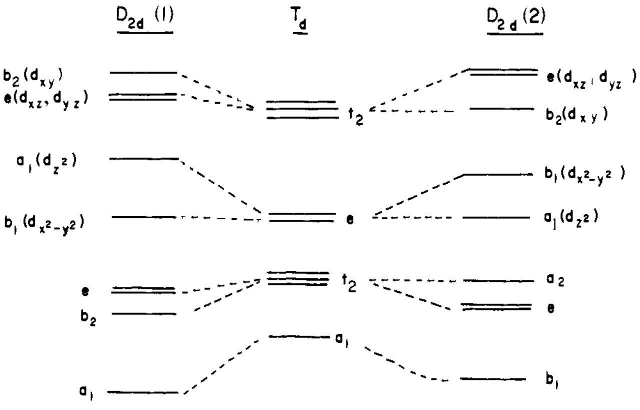

Figure 4. A qualitative MO scheme for M(NR$_2$)$_4$ complexes in two different D_{2d} configurations (see text).

Table III. Computed Ionization Energies for Cr(NH$_2$)$_3$ and Experimental Ionization Energies for Cr(N-i-Pr$_2$)$_3$.

MO	computed IE[a]	exptl IE[a]
4a$_1$	6.76	6.3
6e	7.01	6.53
3a$_2$	7.52	7.38
5e	8.57	7.9
4e 3a$_1$		9.9

[a] All values in eV.

4a$_1$ (71% metal), causing the crossover in the observed UV PES. This type of behavior is characteristic of the UV PES of several transition-metal compounds.[23]

The tetracoordinate dialkylamides of Cr and Mo are of interest because, while both are d^2 systems, Cr(NEt$_2$)$_4$ is paramagnetic yet Mo(NMe$_2$)$_4$ and Mo(NEt$_2$)$_4$ are diamagnetic. If the nitrogen geometry is taken to be trigonal planar and metal-nitrogen bond rotation is assumed to be slow on the UV PES time scale, the maximum skeletal symmetry of a M(NR$_2$)$_4$ compound is D_{2d}. There are, in fact, two possible structures that possess this geometry: D_{2d}(1), in which the C-N-C planes are perpendicular to the dihedral planes, and D_{2d}(2), in which the C-N-C planes are parallel to the dihedral planes. In T_d symmetry the metal nd orbitals split into the familiar e and t$_2$ sets; reduction of symmetry to D_{2d}(1) or D_{2d}(2) results in these orbitals transforming as b$_1$, a$_1$, b$_2$, and e as illustrated in Figure 4. In D_{2d}(1) symmetry the nitrogen lone pair MOs, n$_{\mathrm{N}}$, span the irreducible representations a$_1$, b$_2$, and e, while in D_{2d}(2) symmetry these transform as a$_2$, b$_1$, and e. Dative π-bonding interactions are permitted between the nitrogen lone pair and metal nd MOs of the same symmetry as illustrated. Thus it is clear (Figure 4) that no interactions are possible with the b$_1$ (d$_{x^2-y^2}$) or a$_1$ (d$_{z^2}$) metal and MOs in D_{2d}(1) or D_{2d}(2) symmetry, respectively. These orbitals are the HOMOs in low-spin d^2 systems.

The crystal structure of Mo(NMe$_2$)$_4$ has been investigated recently[24] and the molecule has been found to adopt D_{2d}(1) symmetry. The UV PES of Mo(NMe$_2$)$_4$ (Figure 1b) is consistent with the ground-state electronic configuration . . . (a$_1$)^2(b$_2$)^2(e)^4(b$_1$)^2. Thus, I$_1$ clearly corresponds to ionization of the b$_1$ metal-localized MO, while peaks I$_2$, I$_3$, and I$_4$ can be assigned to electron ejection from the nitrogen lone pair MOs of symmetries e, b$_2$, and a$_1$, respectively on the basis of intensity considerations. The broad, intense peak at 10.7 eV represents ionization of the a$_1$, e, and b$_2$ molybdenum-nitrogen σ-bonding MOs of symmetries a$_1$, e, and b$_2$. The general correctness of this sequence of orbitals has been confirmed by Fenske-Hall calculations on Mo(NMe$_2$)$_4$ which, in addition, revealed that the b$_1$ MO is 97% 4d$_{x^2-y^2}$ in character, and that the e, b$_2$, and a$_1$ MOs comprise 91, 94, and 71% ligand π character, respectively.[24] The low value for I$_1$ (5.30 eV) is consistent with the Fenske-Hall calculations on Mo(NMe$_2$)$_4$ which indicate that the b$_1$ MO is slightly antibonding. The UV PES of Mo(NEt$_2$)$_4$ (Figure 1c) is quite similar to that of Mo(NMe$_2$)$_4$ and can be assigned in an analogous manner. As

Table IV. Ionization Energy Data[a] for $M(NR_2)_4$ and $M(NR_2)_5$ Compounds

	$M(NR_2)_4$	
ionic state	$Mo(NMe_2)_4$	$Mo(NEt_2)_4$
$^2B_1(d_{x^2-y^2})$	5.30	5.3
$^2E(n_N)$	7.34	7.0,[b] 7.3[b]
$^2B_2(n_N)$	7.70	7.56
$^2A_1(n_N)$	9.01	8.7
M-N ionizations	10.7	
	$M(NR_2)_5$	
	$Nb(NMe_2)_5$	$Ta(NMe_2)_5$
n_N	6.77	6.89
	6.9	7.1
	7.63	7.78
	8.02	8.15
	8.21	8.35
M-N ionizations	9.7, 10.2	9.7, 10.4

[a] All values in eV. [b] Splitting due to the Jahn-Teller effect. See text.

expected, the energy required for production of the $^2B_1$ state via electron ejection from the M ($4d_{x^2-y^2}$) orbital is virtually identical in both compounds, and slight inductive shifts are apparent in the IEs associated with the nitrogen lone pair MOs. The somewhat more complex appearance of the spectrum of $Mo(NEt_2)_4$ in the nitrogen lone pair region could be due to (a) the actual symmetry of $Mo(NEt_2)_4$ being lower than that of $Mo(NMe_2)_4$ or (b) an increased Jahn-Teller splitting of the ^2E state in $Mo(NEt_2)_4$ compared to $Mo(NMe_2)_4$.

Interestingly, $Cr(NEt_2)_4$ (Figure 1d) is paramagnetic, although the reasons for this are not clear at the present time. Probably it is a reflection of the spin-pairing energies being in the order Cr > Mo and the ligand field energies being in the order Mo > Cr; alternatively, $Cr(NEt_2)_4$ could adopt the $D_{2d}(2)$ structure. If so, the electronic configuration of the ground state would be $(b_1)^2(e)^4(a_2)^2(a_1)^1(b_1)^1$ rather than $(a_1)^2(b_2)^2(e)^4(b_1)^1(a_1)^1$. The ionic states emerging from the photoionization of both the $D_{2d}(1)$ and $D_{2d}(2)$ ground-state electronic configurations are presented in Table I along with possible spectral assignments. If one argues (probably in an oversimplified way) on the basis of peak intensities, the better fit is obtained with the $D_{2d}(2)$ ground-state structure. However, this conjecture, while interesting, should be viewed cautiously. Clearly, the structure of $Cr(NEt_2)_4$ should be determined.

One of the intriguing aspects of the pentacoordinate amides concerns the apparently close energies of the square-pyramidal and trigonal-bipyramidal MN_5 geometries. Thus, it has been demonstrated by X-ray crystallography that the NbN_5 moiety of $Nb(NMe_2)_5$ approaches a square-pyramidal structure,[25] while $Ta(NEt_2)_4$ has been found to adopt a trigonal-bipyramidal geometry for the TaN_5 skeleton.[26] The UV PES of $Nb(NMe_2)_5$ and $Ta(NMe_2)_5$ are virtually identical (except for a small shift in the absolute value of the IEs) and only the spectrum of the latter is illustrated in Figure 1e. It thus appears that $Nb(NMe_2)_5$ and $Ta(NMe_2)_5$ are isostructural in the vapor phase. In a square-pyramidal (C_2) arrangement of MNC_2 moieties the five peaks in the nitrogen lone pair region would correspond to the ionization of two a and three b MOs. However, it is difficult to be more specific without MO calculations. The lower IEs are, therefore, listed without assignments in Table IV.

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