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A UV PHOTOELECTRON SPECTROSCOPIC INVESTIGATION OF THE BONDING I--ETC(U)

1979 M H CHISHOLM, A H COWLEY, M LATTMAN

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→ compound $\text{Cr}(\text{NH}_2)_3$. In contrast to previous UPS work on $\text{Cr}[\text{N}(\text{SiMe}_3)_2]_3$, ionizations are detectable from the metal MO's of $\text{Cr}(\text{N}^1\text{Pr}_2)_3$. The UPS of the tetracoordinate molybdenum compounds, $\text{Mo}(\text{NR}_2)_4$, $\text{R}=\text{Me}$, Et are in excellent agreement with X-ray crystallographic data on $\text{Mo}(\text{NMe}_2)_4$ and exhibit a low energy ionization (~ 5.3 eV) which is attributable to electron ejection from the essentially pure $\text{Mo } 4d_{(x)^2(-y)^2}$ MO of b_1 symmetry. The pentacoordinate compounds, $\text{M}(\text{NMe}_2)_5$, $\text{M}=\text{Nb}$, Ta exhibit very similar UPS and therefore appear to be isostructural in the vapor phase. ↙

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Abstract: Helium (I) ultraviolet photoelectron spectra (UPS) are reported for the compounds $\text{Cr}(\text{N}^i\text{Pr}_2)_3$, $\text{Cr}(\text{NEt}_2)_4$, $\text{Mo}(\text{NMe}_2)_4$, $\text{Mo}(\text{NEt}_2)_4$, $\text{Nb}(\text{NMe}_2)_5$, and $\text{Ta}(\text{NMe}_2)_5$. The interpretation of the UPS of the paramagnetic dialkylamide, $\text{Cr}(\text{N}^i\text{Pr}_2)_3$, was aided by a SCF X_α scattered wave (X_α SW) calculation on the model compound $\text{Cr}(\text{NH}_2)_3$. In contrast to previous UPS work on $\text{Cr}[\text{N}(\text{SiMe}_3)_2]_3$, ionizations are detectable from the metal MO's of $\text{Cr}(\text{N}^i\text{Pr}_2)_3$. The UPS of the tetracoordinate molybdenum compounds, $\text{Mo}(\text{NR}_2)_4$, $\text{R} = \text{Me}, \text{Et}$ are in excellent agreement with X-ray crystallographic data on $\text{Mo}(\text{NMe}_2)_4$ and exhibit a low energy ionization (~ 5.3 eV) which is attributable to electron ejection from the essentially pure $\text{Mo } 4d_{x^2-y^2}$ MO of b_1 symmetry. The pentacoordinate compounds,

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$M(NMe_2)_5$, $M = Nb, Ta$ exhibit very similar UPS 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 (UPS) because, as shown in previous studies³⁻⁵, the peaks at lower binding energies corresponding to electron ejection from metal-centered MO's, nitrogen lone pair MO's, and metal-nitrogen σ -bonding MO's fall into distinct regions. The UPS 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 UPS of $\text{Cr}(\text{N}^i\text{Pr}_2)_3$, $\text{Cr}(\text{NEt}_2)_4$, $\text{Mo}(\text{NMe}_2)_4$, $\text{Mo}(\text{NEt}_2)_4$, $\text{Nb}(\text{NMe}_2)_5$ and $\text{Ta}(\text{NMe}_2)_5$. Our interest in the tricoordinate species, $\text{Cr}(\text{N}^i\text{Pr}_2)_3$, was generated by the fact that in the corresponding silylamide, $\text{Cr}[\text{N}(\text{SiMe}_3)_2]_3$, it was impossible to detect UPS peaks corresponding to the ionization of metal-localized MO's.⁵ The tetracoordinate dialkylamides, $\text{Cr}(\text{NEt}_2)_4$ and $\text{Mo}(\text{NR}_2)_4$, $\text{R} = \text{Me}, \text{Et}$, are the first Group VI A amides to be studied by UPS; particular interest is associated with these compounds because the molybdenum amides are diamagnetic yet $\text{Cr}(\text{NEt}_2)_4$ is paramagnetic. Finally, the pentacoordinate amides, $\text{M}(\text{NMe}_2)_5$, $\text{M} = \text{Nb}, \text{Ta}$, 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 X_α scattered-wave calculation⁶ (hereafter referred to as X_α SW) has been performed on the model amide $\text{Cr}(\text{NH}_2)_3$ to facilitate the interpretation of the UPS data. As is well known, this theoretical approach has the advantage of avoiding the use of Koopmans' theorem⁷ by means of the transition state method⁸.

EXPERIMENTAL SECTION

Materials. The compounds $\text{Cr}(\text{N}^i\text{Pr}_2)_3$ ⁹, $\text{Cr}(\text{NEt}_2)_4$ ¹⁰, $\text{Mo}(\text{NMe}_2)_4$ ¹¹, $\text{Mo}(\text{NEt}_2)_4$ ¹¹, $\text{Nb}(\text{NMe}_2)_5$ ¹², and $\text{Ta}(\text{NMe}_2)_5$ ¹³ were prepared and purified as described in the literature.

Spectroscopic Measurements. All UPS 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.

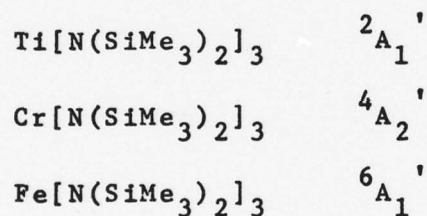
Computational Procedures. The X_α SW calculation on $\text{Cr}(\text{NH}_2)_3$ was made by employing the spin-restricted procedure of Johnson and Slater⁶, setting the occupation numbers of the 6e and 4a₁ levels at two and one, respectively, in accord with the

observed ground state electronic configuration.⁹ The bond distances and angles for $\text{Cr}(\text{NH}_2)_3$ were based on those observed by X-ray crystallography for $\text{Cr}(\text{N}^i\text{Pr}_2)_3$,¹⁴ except 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 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 $\ell = 2$ were employed for the chromium and outer spheres, while functions through $\ell=1$ and $\ell=0$ 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 IE's for $\text{Cr}(\text{NH}_2)_3$ were computed by the transition state method⁸.

RESULTS AND DISCUSSION

The tricoordinate compounds, $\text{M}[\text{N}(\text{SiMe}_3)_2]_3$, $\text{M}=\text{Ti}, \text{Cr}, \text{Fe}$, and $\text{Cr}(\text{N}^i\text{Pr}_2)_3$ represent examples of the stabilization of low coordination numbers by means of bulky groups. Single

crystal X-ray structures of $\text{Fe}[\text{N}(\text{SiMe}_3)_2]_3$ ¹⁷ and $\text{Cr}(\text{N}^i\text{Pr}_2)_3$ 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 data¹⁹, and crystal field calculations¹⁹ indicate that the ground state electronic configurations of the silylamides are



The dialkylamide, $\text{Cr}(\text{N}^i\text{Pr}_2)_3$, has been shown⁹ to have the same ground state electronic configuration as $\text{Cr}[\text{N}(\text{SiMe}_3)_2]_3$.

Curiously, despite the presence of unpaired electrons in the above silylamides no low energy ionizations attributable to metal-localized orbitals were detectable in the UPS⁵.

The reason which was advanced for this phenomenon is that the metal MO's are stabilized significantly by the more electron-withdrawing $(\text{Me}_3\text{Si})_2\text{N}$ groups, possibly causing them to be of comparable energies to the nitrogen lone pair MO's. Interestingly, $\text{Cr}(\text{N}^i\text{Pr}_2)_3$ does exhibit peaks at low IE which can be attributed to the ionization of metal-localized MO's (Figure 1a). The detailed assignment of the UPS 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 $\text{Cr}(3d)$ orbitals of a_2 and e symmetry, respectively (see below). In threefold symmetry the nitrogen "lone pair" MO's span the a_2 and e irreducible representations. However, as is clear from the nodal properties of such MO's (Figure 2) their relative energies are sensitive to the dihedral angle.²² Obviously, at intermediate values of ϕ , a "cross-over" occurs, and, at some particular value of ϕ the a_2 and e MO's must be degenerate. Since the dihedral angle between the CrN_3 and NC_2 planes is 71° in $\text{Cr}(\text{N}^i\text{Pr}_2)_3$ 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 MO's 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 MO's (of symmetry a_1 and e); however, it is difficult to advance specific assignments.

The foregoing, qualitative interpretation of the UPS of $\text{Cr}(\text{N}^{\text{I}}\text{Pr}_2)_3$ is in good accord with the X_α SW calculation on the model compound $\text{Cr}(\text{NH}_2)_3$ (Tables II and III). Thus, the two highest occupied MO's (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 MO's are both mainly nitrogen lone pair; 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 wavefunction in Figure 3a shows nitrogen lone pair overlap with the Cr $3d_{xy}$ orbital. The next two MO's, 4e and $3a_1$, are the σ -bonding orbitals of the molecule. The contour of one of the degenerate 4e wavefunctions 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 MO's, $2a_2$, 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 IE's (Table III) for the $4a_1$ and $6e$ metal-localized MO's 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 $4a_1$ (71% metal), causing the crossover in the observed UPS. This type of behavior is characteristic of the UPS 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 UPS 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 MO's, n_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 MO's 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 MO's in $D_{2d}(1)$ or $D_{2d}(2)$ symmetry, respectively. These orbitals are the HOMO's in low spin d^2 systems.

The crystal structure of $Mo(NMe_2)_4$ has been investigated recently²⁴ and the molecule has been found to adopt $D_{2d}(1)$ symmetry. The UPS 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 MO's 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 MO's 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 MO's

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 $\text{Mo}(\text{NMe}_2)_4$ which indicate that the b_1 MO is slightly antibonding. The UPS of $\text{Mo}(\text{NEt}_2)_4$ (Figure 1c) is quite similar to that of $\text{Mo}(\text{NMe}_2)_4$ and can be assigned in an analogous manner. As expected the energy required for production of the 2B_1 state via electron ejection from the $\text{Mo}(4d_{x^2-y^2})$ orbital is virtually identical in both compounds, and slight inductive shifts are apparent in the IE's associated with the nitrogen lone pair MO's. The somewhat more complex appearance of the spectrum of $\text{Mo}(\text{NEt}_2)_4$ in the nitrogen lone pair region could be due to (a) the actual symmetry of $\text{Mo}(\text{NEt}_2)_4$ being lower than that of $\text{Mo}(\text{NMe}_2)_4$, or (b) an increased Jahn/Teller splitting of the 2E state in $\text{Mo}(\text{NEt}_2)_4$ compared to $\text{Mo}(\text{NMe}_2)_4$.

Interestingly, $\text{Cr}(\text{NEt}_2)_4$ (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 $\text{Cr} > \text{Mo}$ and the ligand field energies being in the order $\text{Mo} > \text{Cr}$; alternatively, $\text{Cr}(\text{NEt}_2)_4$ 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 $\text{Cr}(\text{NEt}_2)_4$ 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 $\text{Nb}(\text{NMe}_2)_5$ approaches a square pyramidal structure²⁵, while $\text{Ta}(\text{NEt}_2)_5$ has been found to adopt a trigonal bipyramidal geometry for the TaN_5 skeleton.²⁶ The UPS of $\text{Nb}(\text{NMe}_2)_5$ and $\text{Ta}(\text{NMe}_2)_5$ are virtually identical (except for a small shift in the absolute value of the IE's) and only the spectrum of the latter is illustrated in Figure 1e. It thus appears that $\text{Nb}(\text{NMe}_2)_5$ and $\text{Ta}(\text{NMe}_2)_5$ 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 MO's. However, it is difficult to be more specific without MO calculations. The lower IE's are, therefore, listed without assignments in Table IV.

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REFERENCES AND NOTES

- (1) (a) Indiana University; (b) University of Texas at Austin.
- (2) For reviews, see (a) D. C. Bradley, *Adv. Inorg. Chem. Radiochem.*, **15**, 259 (1972); (b) D. C. Bradley and M. H. Chisholm, *Acc. Chem. Res.*, **9**, 273 (1976).
- (3) S. G. Gibbins, M. F. Lappert, J. B. Pedley, and G. J. Sharp, *J. Chem. Soc. Dalton Trans.*, 72 (1975).
- (4) D. H. Harris, M. F. Lappert, J. B. Pedley, and G. J. Sharp, *J. Chem. Soc. Dalton Trans.*, 945 (1976).
- (5) M. F. Lappert, J. B. Pedley, G. J. Sharp, and D. C. Bradley, *J. Chem. Soc. Dalton Trans.*, 1737 (1976).
- (6) J. C. Slater, *Adv. Quantum Chem.*, **6**, 1 (1972); (b) K. H. Johnson, *ibid.*, **7**, 143 (1973); (c) K. H. Johnson, *Annu. Rev. Phys. Chem.*, **26**, 39 (1975).
- (7) T. Koopmans, *Physica*, **1**, 104 (1934).
- (8) (a) J. C. Slater and K. H. Johnson, *Phys. Rev.*, **B**, **5**, 844 (1972); (b) J. C. Slater, Quantum Theory of Molecules and Solids, Vol. 4, McGraw-Hill, New York, 1974, p. 583.
- (9) E. C. Alyea, J. S. Basi, D. C. Bradley, and M. H. Chisholm, *Chem. Commun.*, 495 (1968).
- (10) J. S. Basi and D. C. Bradley, *Proc. Chem. Soc. Landau*, 305 (1963).
- (11) D. C. Bradley and M. H. Chisholm, *J. Chem. Soc. A*, 274 (1971).
- (12) D. C. Bradley and I. M. Thomas, *Can. J. Chem.*, **40**, 449 (1962).
- (13) D. C. Bradley and I. M. Thomas, *Can. J. Chem.*, **40**, 1355 (1962).

- (14) D. C. Bradley, M. B. Hursthouse, and C. W. Newing, *Chem. Commun.*, 411 (1971).
- (15) (a) J. G. Norman, *J. Chem. Phys.*, **61**, 4630 (1974);
(b) J. G. Norman, *Mol. Phys.*, **31**, 1191 (1976). (c) $r_{cr} = 2.586$, $r_N = 1.136$, $r_H = 0.7724$, $r_{OUTER} = 5.537$ (in a.u.).
- (16) (a) K. Schwartz, *Phys. Rev.*, B **5**, 2466 (1972). (b) J. C. Slater, *Int. J. Quantum Chem.*, **1**, 533 (1973).
- (17) D. C. Bradley, M. B. Hursthouse, and P. F. Rodesiler, *Chem. Commun.*, 14 (1969).
- (18) (a) D. C. Bradley and R. G. Copperthwaite, *Chem. Commun.*, 764 (1971). (b) E. C. Alyea, D. C. Bradley, R. G. Copperthwaite, K. D. Sales, B. W. Fitzsimmons, and C. E. Johnson, *Chem. Commun.*, 1715 (1970).
- (19) E. C. Alyea, D. C. Bradley, R. C. Copperthwaite, and K. D. Sales, *J. Chem. Soc. Dalton Trans.*, 185 (1973).
- (20) P. A. Cox and A. F. Orchard, *Chem. Phys. Lett.*, **7**, 273 (1970).
- (21) S. Cradock, E. A. V. Ebsworth, and A. Robertson, *J. Chem. Soc. Dalton Trans.*, 22 (1973).
- (22) For a discussion on this point, see A. H. Cowley, *Phosphorus and Sulfur*, **2**, 283 (1976).
- (23) For a review of the UPS of transition metal compounds, see A. H. Cowley, Progress in Inorganic Chemistry,
- (24) M. H. Chisholm, F. A. Cotton, and M. W. Extine, *Inorg. Chem.*, **17**, 1329 (1978).
- (25) C. E. Heath and M. B. Hursthouse, *Chem. Commun.*, 143 (1971).
- (26) R. J. Smallwood, Ph.D. Thesis, University of London, 1975.

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

<u>Ground State</u>	<u>Cr(NⁱPr₂)₃</u> <u>Ion Configuration</u>	<u>Ionic State</u> <u>Produced</u>	<u>Experimental</u> <u>Ionization</u> <u>Energies^a</u>
$e^4 a_2^2 a_1^1 e^2 [^4A_2]$	$e^4 a_2^2 a_1^1 e^1$	3E	6.53
	$e^4 a_2^2 e^2$	3A_2	6.3
	$e^4 a_2^1 a_1^1 e^2$	3A_1 5A_1	7.38
	$e^3 a_2^2 a_1^1 e^2$	3E 5E	7.9
			9.9 (M-Nσ)
$a_1^2 b_2^2 e^4 b_1^1 a_1^1 [^3B_1]$	$a_1^2 b_2^2 e^4 b_1^1$	2B_1	5.9
	$a_1^2 b_2^2 e^4 a_1^1$	2A_1	6.3
	$a_1^2 b_2^2 e^3 b_1^1 a_1^1$	2E 4E	7.0
	$a_1^2 b_2^1 e^4 b_1^1 a_1^1$	2A_2 4A_2	7.2
	$a_1^1 b_2^2 e^4 b_1^1 a_1^1$	2B_1 4B_1	7.9
			10.0 (M-Nσ)

Table I. (cont'd.)

<u>Cr(NEt₂)₄, D_{2d}(2)</u>			
$b_1^2 e^4 a_2^2 a_1^1 b_1^1$ [³ B ₁]	$b_1^2 e^4 a_2^2 a_1^1$	² A ₁	5.9
	$b_1^2 e^4 a_2^2 b_1^1$	² B ₁	6.3
	$b_1^2 e^4 a_2^1 a_1^1 b_1^1$	² B ₂ }	7.0
		⁴ B ₂ }	
	$b_1^2 e^3 a_2^2 a_1^1 b_1^1$	² E }	7.2
		⁴ E }	
	$b_1^1 e^4 a_2^2 a_1^1 b_1^1$	² A ₁ }	7.9
		⁴ A ₁ }	

^aAll values in eV.

Table II. X_α SW "Ground State" Eigenvalues and Charge Densities^a for $\text{Cr}(\text{NH}_2)_3$

MO	ϵ^b	Cr			N			H		OUTER ^c		INT ^d	
		s	p	d	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	0.00		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	0.01		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	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

Table III. Computed Ionization Energies for $\text{Cr}(\text{NH}_2)_3$ and
Experimental Ionization Energies for $\text{Cr}(\text{N}^1\text{Pr}_2)_3$.

<u>MO</u>	<u>Computed IE^a</u>	<u>Experimental IE^a</u>
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

^aAll values in eV.

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

<u>Ionic State</u>	<u>$M(NR_2)_4$</u>	
	<u>$Mo(NMe_2)_4$</u>	<u>$Mo(NEt_2)_4$</u>
$^2B_1(d_{x^2-y^2})$	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	

	<u>$M(NR_2)_5$</u>	
	<u>$Nb(NMe_2)_5$</u>	<u>$Ta(NMe_2)_5$</u>
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

^aAll values in eV

^bSplitting due to the Jahn-Teller effect. See text.

Figure Captions

Figure 1. He(I) UPS of : (a) $\text{Cr}(\text{N}^i\text{Pr}_2)_3$; (b) $\text{Mo}(\text{NMe}_2)_4$; (c) $\text{Mo}(\text{NEt}_2)_4$; (d) $\text{Cr}(\text{NEt}_2)_4$; and (e) $\text{Ta}(\text{NMe}_2)_5$.

Figure 2. Horizontal ($\text{D}_{3h}(1)$, $\phi=90^\circ$) and vertical ($\text{D}_{3h}(2)$, $\phi=90^\circ$) arrangements of N(2p) AO's in threefold symmetry.

Figure 3. X_α SW contour plots for the following MO's of $\text{Cr}(\text{NH}_2)_3$: (a) one of the two degenerate 5e wavefunctions (CrN_3 plane); (b) one of the two degenerate 4e wavefunctions (CrN_3 plane); (c) the $3a_1$ wavefunction (perpendicular to CrN_3 plane, along CrN bond). Contour values are: $1=\pm 0.20$; $2=\pm 0.10$; $3=\pm 0.05$; $4=\pm 0.02$.

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

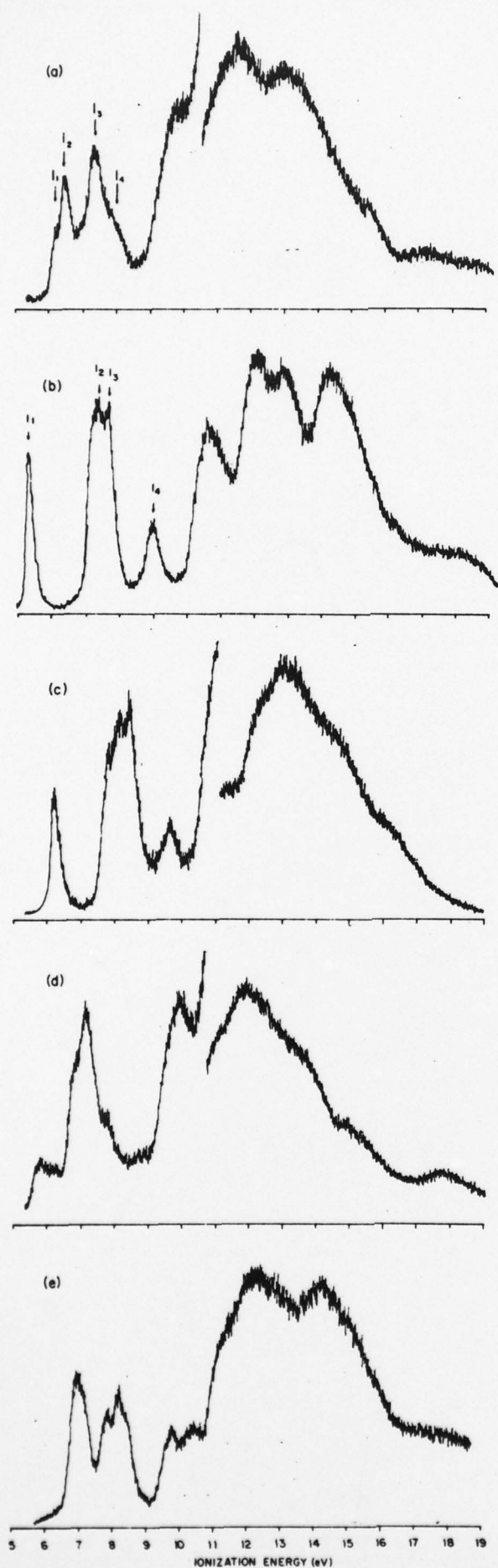


Figure 1

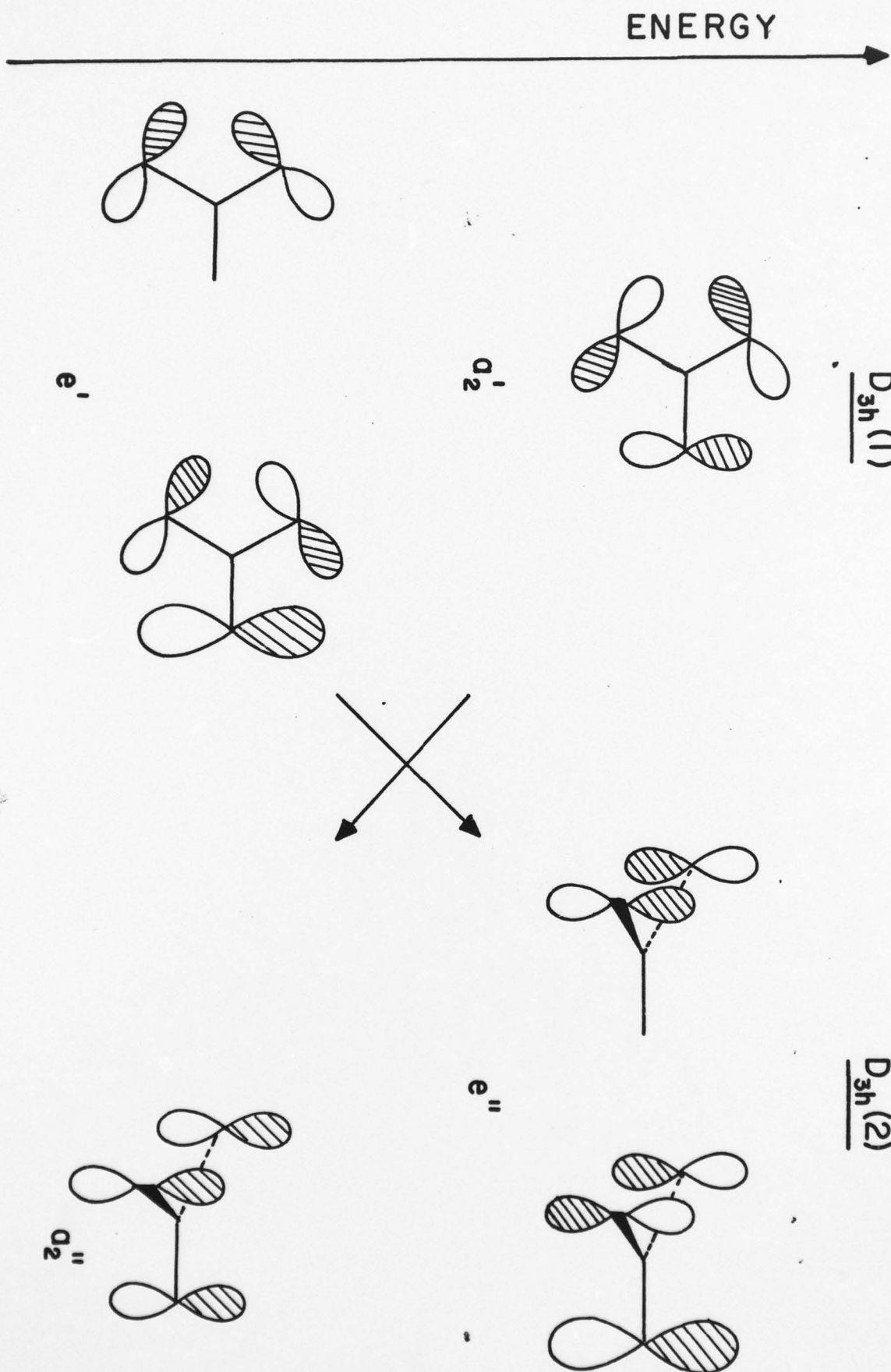


Figure 2

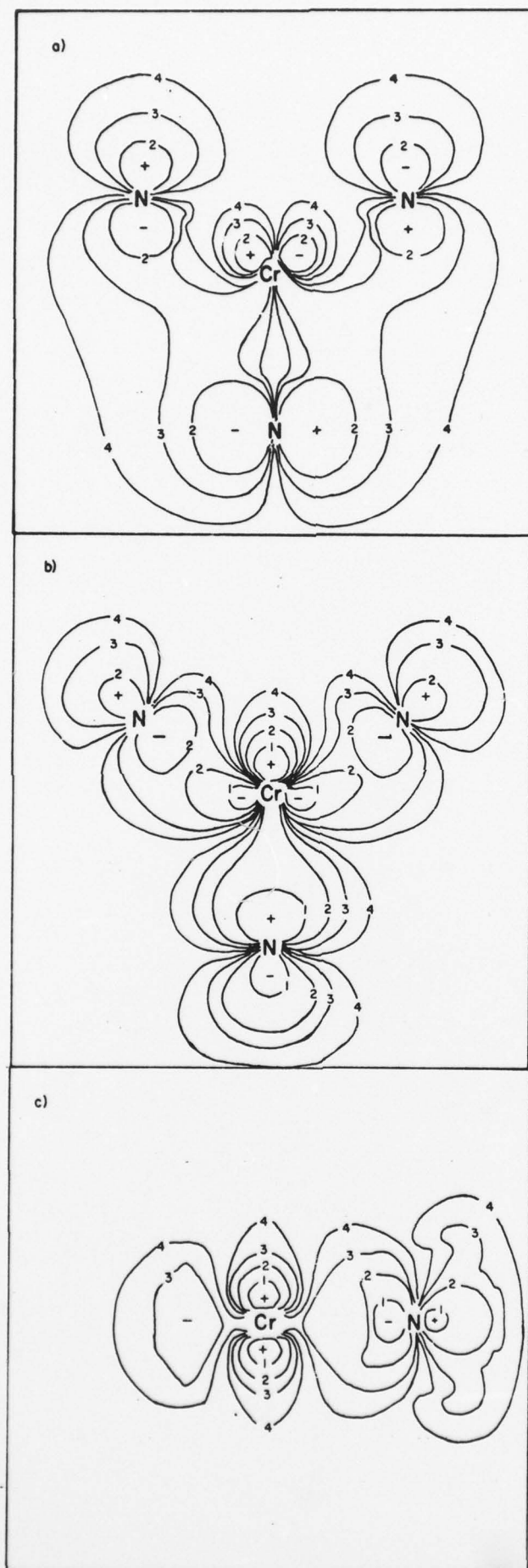


Figure 3

$D_{2d} (1)$

T_d

$D_{2d} (2)$

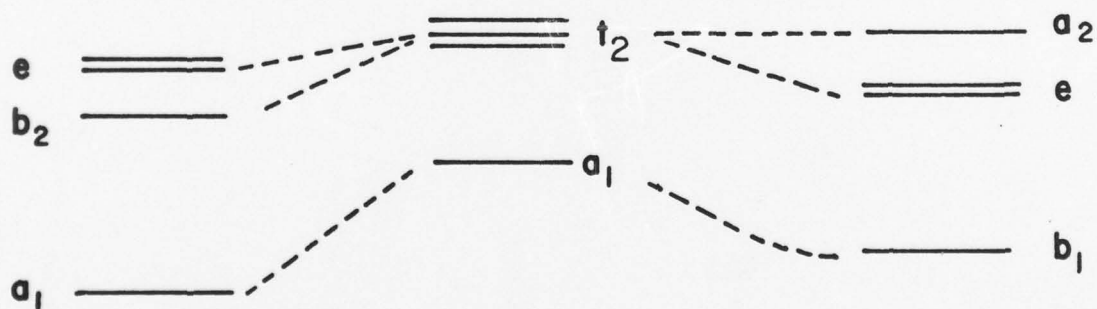
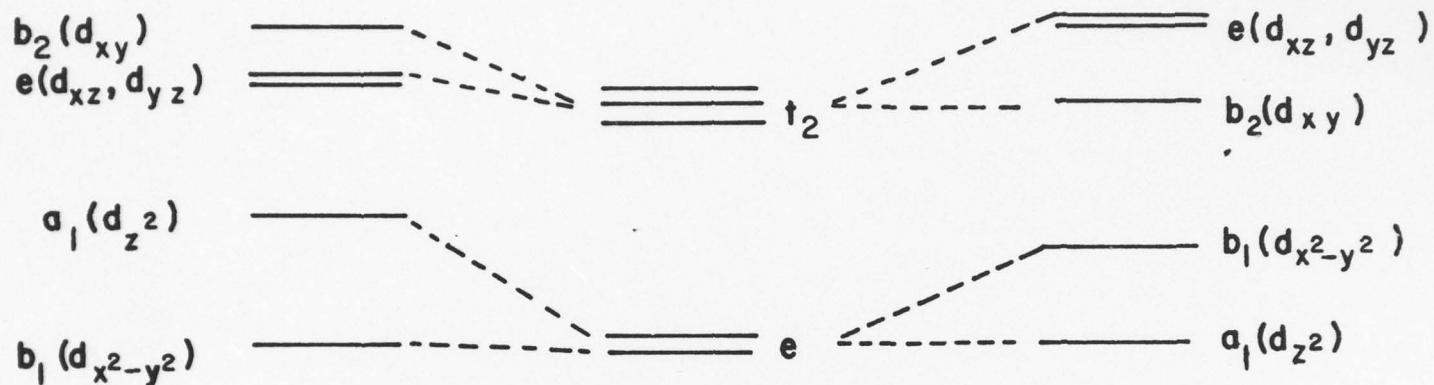


Figure 4

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