Bonding Studies of Transition-metal Complexes. Part II.[1] Helium-I Photoelectron Spectra of Homoleptic d^0, d^1, and d^{10} Tetrakis(dialkylamides) of Transition and Group 4B Metals and Tungsten Hexakis(dimethylamide)

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He(I) Photoelectron (p.e.) spectra of the compounds $M(NR_2)_4$ (M = C, Si, Ge, Sn, Ti, Zr, Hf, or V; R = Me), $M'(NR'_2)_4$ (M' = Ti, Zr, or Hf; R = Et), and $W(NMe_2)_6$ have been measured. The first band(s) in all spectra [except that of $V(NMe_2)_4$ which has a lone *d* electron] have been assigned to ionisation from molecular orbitals (m.o.s) regarded as linear combinations of the nitrogen 'lone-pair' atomic orbitals (a.o.s). The next band corresponds to the main σ(M–N) bonding orbital, while there is an unresolved collection of peaks to higher ionisation potential (i.p.) corresponding to ionisation from the $-NR_2$ bonding m.o.s. From the form of the nitrogen 'lone-pair' section of the spectra it is possible to infer structural information about the molecules.

In Part I we described the p.e. spectra of some d^0 homoleptic metal alkyls MR'_4 (M = Ti, Zr, or Hf; $R' = Me_3CCH_2$ or Me_3SiCH_2) and compared these with those of related, essentially isostructural, Main-group element d^{10} compounds (M = Ge or Sn).[1] We now report results on the dialkylamides $M(NR_2)_4$ [M = C, Si, Ge, Sn, Ti, Zr, Hf, or V; R = Me or (for Ti, Zr, or Hf) Et] and $W(NMe_2)_6$. Homoleptic metal alkyls or dialkylamides provide rare examples of extensive series of volatile transition-metal compounds, especially the type MX_4, which being of relatively high symmetry are suitable for p.e. spectroscopic investigation. [Other known transition-metal tetrakis(dialkylamides) are of Nb, Ta, Cr, Mo, Th, and U.[2]] Further reasons for our interest in the p.e. spectra of metal dialkylamides derive from earlier synthetic,[3] thermochemical,[4] and spectroscopic (including p.e. spectra of boron compounds [5]) studies on such compounds.[6]

The first transition-metal amide to have been made was $Ti(NPh_2)_4$ in 1935,[7] but significant activity in this field was delayed until simpler derivatives became available, beginning with $Ti(NMe_2)_4$ in 1960.[8] Further developments owe much to the synthetic, spectroscopic, and structural studies of D. C. Bradley [2] and H. Bürger [9] and their co-workers. An interesting structural feature of metal dialkylamides is that nonbridging NR_2 groups invariably have trigonal-planar nitrogen atoms, which has been taken as implying M–N π-character,  $\text{M}\!-\!\ddot{\text{N}}\!< \;\longleftrightarrow\; \overset{-}{\text{M}}\!=\!\overset{+}{\text{N}}\!<$. Electronic-absorption spectra of transition-metal derivatives show a substantial ligand-field-splitting energy for NR_2^-. The e.s.r. spectra of V^{IV} and Nb^{IV} dialkylamides have been interpreted as suggesting that the M–N bond is essentially covalent. On the other hand, the high reactivity of metal amides has been interpreted as involving a weak and highly polar M–N bond. Thermochemical data are sparse, but from $\Delta H_f^\ominus$ results $\bar{D}$(M–N) has been estimated as (kcal mol^{-1}) † 63 (CN),[10] 78 [SiN in $Me_3Si(NMe_2)$],[11] 55 [in $Me_3Ge(NMe_2)$],[4] 41 [in $Me_3Sn(NMe_2)$],[4] and *ca.* 73 [in $Ti(NEt_2)_4$].[12] Electron diffraction shows $Sn(NMe_2)_4$ to have skeletal MN_4 T_d symmetry,[13] and vibrational studies suggest a similar feature for the d^0 complexes in solution.[2,14] E.s.r. spectra of $V(NR_2)_4$ show a D_{2d} distorted-tetrahedral VN_4 structure.[15] *X*-Ray diffraction demonstrates T_h heavy-atom symmetry for $W(NMe_2)_6$ with coplanar *trans*-C_2NWNC_2 units.[16]

The objective of this investigation was to determine occupied valence molecular orbital (m.o.) energy levels, and to make assignments, for the structurally related series of closed shell d^0 and d^{10} complexes $M(NR_2)_4$. The d^1 V complex was included as the simplest case of an open-shell analogue, and $W(NMe_2)_6$ because of its interesting symmetry. Although the p.e. spectrum of WMe_6 has been recorded,[17] $W(NMe_2)_6$ is a rare example of a structurally authenticated six-co-ordinate complex to be considered by p.e. study.

EXPERIMENTAL

The compounds $Si(NMe_2)_4$, $Sn(NMe_2)_4$, $Ti(NEt_2)_4$, $Zr(NEt_2)_4$, and $Hf(NEt_2)_4$ were obtained commercially; $Ti(NMe_2)_4$, $Zr(NMe_2)_4$, $Hf(NMe_2)_4$, $V(NMe_2)_4$, and $Ge(NMe_2)_4$ were synthesised by published procedures.[2] We

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† 1 cal = 4·184 J.

[1] Part I, M. F. Lappert, J. B. Pedley, and G. J. Sharp, *J. Organometallic Chem.*, 1974, **66** 271.

[2] *cf.*, D. C. Bradley, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 259.

[3] *cf.*, M.F. Lappert and A. R. Sanger, *J. Chem. Soc.* (*A*), 1971, 1314, and earlier papers in that series.

[4] *cf.*, J. C. Baldwin, M. F. Lappert, J. B. Pedley, and J. S. Poland, *J.C.S. Dalton*, 1972, 1943, and earlier papers in that series.

[5] *cf.*, G. H. King, S. S. Krishnamurthy, M. F. Lappert, and J. B. Pedley, *Faraday Discuss Chem. Soc.*, 1972, **70**, no. 54, and earlier papers in that series.

[6] *cf.*, M. F. Lappert, Tilden Lecture, 1973.

[7] D. C. Dermer and W. C. Fernelius, *Z. anorg. Chem.*, 1935, **221**, 83.

[8] D. C. Bradley and I. M. Thomas, *J. Chem. Soc.*, 1960, 3857.

[9] H. Bürger and U. Wannagat, *Monatsh.*, 1963, **94**, 1007 [the first paper reporting a transition-metal complex of the $(Me_3Si)_2N^-$ ligand, $Fe\{N(SiMe_3)_2\}_3$].

[10] *cf.*, J. D. Cox and G. Pilcher 'Thermochemistry of Organic and Organometallic Compounds,' Academic Press, New York, 1970.

[11] J. C. Baldwin, M. F. Lappert, J. B. Pedley, and J. A. Treverton, *J. Chem. Soc.* (*A*), 1967, 1980.

[12] D. C. Bradley and M. J. Hillyer, *Trans. Faraday Soc.*, 1966, **62**, 2374.

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[15] C. E. Holloway, F. E. Mabbs, and W. R. Smail, *J. Chem. Soc.* (*A*), 1968, 2980; D. C. Bradley, R. H. Moss, and K. D. Sales, *Chem. Comm.*, 1969, 1255.

[16] D. C. Bradley, M. H. Chisholm, C. E. Heath, and M. B. Hursthouse, *Chem. Comm.*, 1969, 1261.

[17] S. S. Cradock and W. Savage, *Inorg. Nuclear Chem. Letters*, 1972, 753.

thank Professor D. C. Bradley for a gift of $W(NMe_2)_6$, and Mr. K. Turner for preparing a sample of $C(NMe_2)_4$. All compounds were fractionally distilled before use and their purity was checked by i.r. and ^1H n.m.r. spectroscopic methods and microanalyses.

Spectra were recorded on a Perkin-Elmer PS 16 He(I) p.e. spectrometer. Two different methods of admitting the sample were employed: for the less-volatile amides the inserted-probe method was used, while the more volatile compounds were bled in remotely. Instrumental resolution varied from 20 to 50 meV, and the number of counts from 150 to 10^4 counts s^{-1}. Spectra were calibrated using methyl iodide and argon.

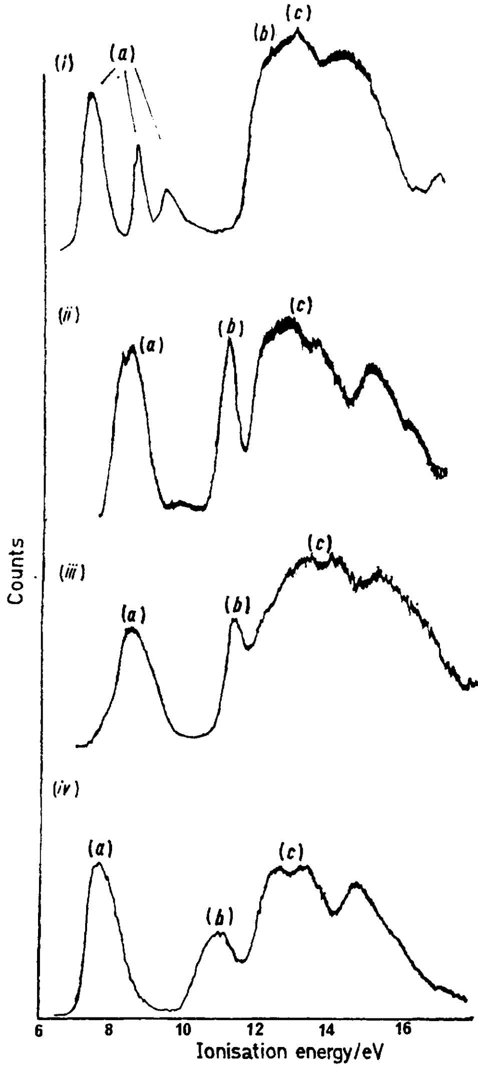

FIGURE 1 He(I) p.e. spectra of $M(NMe_2)_4$: M = C (*i*), Si (*ii*), Ge (*iii*), and Sn (*iv*)

RESULTS AND DISCUSSION

The spectra are shown in Figures 1—4, and the vertical ionisation potentials (i.p.s) are recorded in Table 1, correlating equivalent i.p.s where possible. The spectra of the Group 4B dimethylamides will be discussed initially. On the basis of the results so obtained, the

TABLE 1

Energies (vertical i.p. in eV) of the highest-occupied m.o.s in some metal dialkylamides

	Assignment				
Compound	Lone-pair region section [(*a*)]				M–N Bonding region section [(*b*)]
(Me_2NH [a]	8·85)				
$C(NMe_2)_4$	7·19	8·43	9·20		Unresolved
$Si(NMe_2)_4$	8·69				11·21
$Ge(NMe_2)_4$	8·48				11·16
$Sn(NMe_2)_4$	7·67				10·84
$V(NMe_2)_4$ [b]	7·08	7·60	8·28		10·41
$Ti(NMe_2)_4$	7·13	7·36	7·75	8·00	10·32
$Zr(NMe_2)_4$	7·23	7·54	7·92	8·14	10·44
$Hf(NMe_2)_4$	7·50	7·82	8·05	8·34	10·56
(Et_2NH [a]	8·68)				
$Ti(NEt_2)_4$	6·83	7·10	7·47	7·75	9·78
$Zr(NEt_2)_4$	6·76	6·98	7·35	7·54	9·55
$Hf(NEt_2)_4$	7·15	7·35	7·68	7·91	9·97
$W(NMe_2)_6$	6·73	7·92			9·55 9·95

[a] Spectra not shown. [b] d^1 Electron at 6·2 eV.

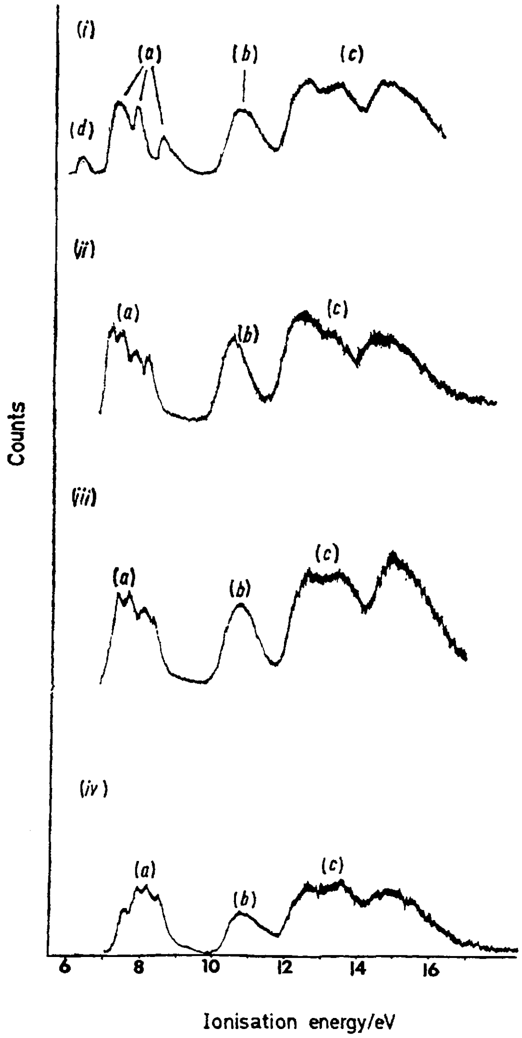

FIGURE 2 He(I) p.e. spectra of $M(NMe_2)_4$: M = V (*i*), Ti (*ii*), Zr (*iii*), and Hf (*iv*)

Group 4A diethylamides and the Group 4A and vanadium dimethylamides will then be considered. Finally, a

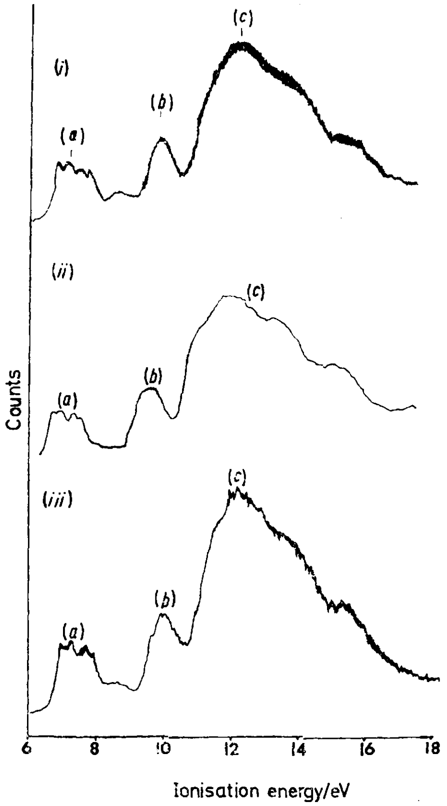

FIGURE 3 He(I) p.e. spectra of $M(NEt_2)_4$: M = Ti (*i*), Zr (*ii*), Hf (*iii*)

tentative assignment of the p.e. spectrum of tungsten hexakis(dimethylamide) will be proposed.

The Molecules $M(NR_2)_4$.—*Introduction.* The $M(NC_2)_4$ framework is considered first. Structural studies have shown that the nitrogen atoms are tetrahedrally disposed about the central Group 4 atom.[2] If there is free

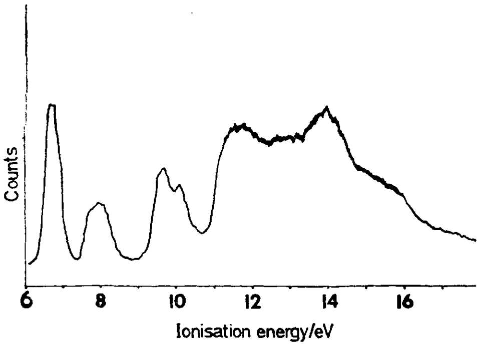

FIGURE 4 He(I) p.e. spectrum of $W(NMe_2)_6$

rotation about the M–N bonds, then the symmetry of the $M(NC_2)_4$ fragment is T_d. If, on the other hand, the carbon atoms are fixed, then the position of minimum steric hindrance is that shown in Figure 5, with the $M(NC_2)_4$ framework having D_{2d} symmetry. The p.e. spectra were consistent with this conformation. For the closed-shell molecules, the spectra consisted of three characteristic sections, marked (*a*), (*b*), and (*c*) in Figures 1—4; for the d^1 vanadium dimethylamide, ionisation of the lone *d* electron was observed at low i.p. Section (*c*) of the spectra corresponds to ionisations from the C–H and $>$N–Me orbitals and, as it consists substantially of a broad series of unresolved bands, is not discussed further. Section (*b*) of the spectra is assigned to ionisation from the M–N bonds, and (*a*) to ionisation from the nitrogen lone-pair orbital.

Group 4B *amides*. The spectra of these compounds showed an essentially symmetric band [section (*b*)] which is assigned to ionisation from a central atom–nitrogen bonding m.o. of symmetry T_2 (assuming T_d local symmetry around the metal). Such a band is a characteristic of other Group 4 MX_4 compounds, such as MR_4.[1,18] The i.p. of this m.o. is expected to decrease monotonically down the Group in accordance with the lower i.p.s of the increasingly heavier central atom. It was not possible to locate an m.o. of A_1 symmetry; it is likely that this is concealed by other ionisations in section (*c*). It is instructive to compare the i.p.s of the T_2 central atom–ligand m.o.s of $M(NR_2)_4$ and

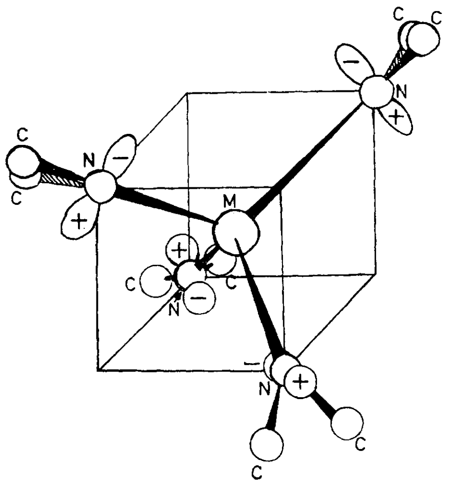

FIGURE 5 Diagram of $M(NC_2)_4$ framework showing nitrogen ' lone pairs ' in the A_1 combination

MMe_4, as shown in Table 2. From these data, extrapolation suggests that for $C(NMe_2)_4$ the t_2 m.o. is concealed by the broad bands due to $-\mathrm{N}{<}^{\mathrm{Me}}_{\mathrm{Me}}$ ionisations, section (*c*). This assumption is central in our assignment of the lone-pair bands.

The bands of lowest i.p. [section (*a*)] in these compounds are attributed to ionisation from the lone-pair orbitals on the four nitrogen atoms. If these orbitals

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[18] S. Evans, J. C. Green, P. J. Joachim, A. F. Orchard, D. W. Turner, and J. P. Maier, *J.C.S. Faraday II*, 1972, 905; R. Boschi, M. F. Lappert, J. B. Pedley, W. Schmidt, and B. T. Wilkins, *J. Organometallic Chem.*, 1973, **50**, 69.

are non-interacting, either by being too far apart or because of free rotation, then a single peak should be observed. If, on the other hand, the conformation of the molecule is locked in D_{2d} symmetry, the nitrogen orbitals interact to give E, B_1, and A_1 combinations. Figure 5 shows the four lone pairs in the A_1 combination.

TABLE 2

Energies (vertical i.p.s) of highest-energy metal–ligand m.o.s of T_2 symmetry in some Group 4 dialkylamides and methyls, MX_4

M–X	I.p.[a]/eV	M–X	I.p.[b]/eV
C–N	Not observed	C–C	11·1
Si–N	11·2	Si–C	10·6
Ge–N	11·0	Ge–C	10·3
Sn–N	10·8	Sn–C	9·7

[a] This work. [b] See ref. 18.

Experimentally, excepting in $C(NMe_2)_4$, only a very small splitting of the first band was observed. The spectrum of $C(NMe_2)_4$ showed three distinct and well separated bands in section (*a*), with intensity ratios *ca.* 2 : 1 : 1. Although strictly there is no relation between the degeneracy of an orbital and the intensity of the p.e. band, such a relation is often used in the interpretation of p.e. spectra. Here there are three bands with intensity ratios 2 : 1 : 1 and we consider that they correspond to the E, B_1, and A_1 symmetry combinations of the nitrogen lone pairs respectively. The lone-pair orbitals in $C(NMe_2)_4$ are thus assigned to these respective symmetry combinations, in order of increasing i.p. Hence, either all four components in the heavier amides are almost degenerate due to little interaction, or free rotation is occurring making the four components degenerate. (It seems certain that the first band contains all the four lone pairs, since it is unlikely that a nitrogen lone pair has an i.p. above 10·5 eV.) * Both factors probably play a role. Thus, as the C–N bond length is considerably shorter than Si–N, Ge–N, or Sn–N, a considerably greater interaction would be expected between the lone-pair orbitals in CN_4 than in the latter compounds. Restriction to rotation about the M–N bond is expected also to be a function of bond length, although bond strengths (see below) do not fall monotonically (CN < SiN > GeN > SnN); [11] in any event, rotation about the Sn–N bonds is likely to be least hindered. The silicon and tin amides showed a slight splitting of the lone-pair band of the order of 200 meV.

Group 4A *amides and* $V(NMe_2)_4$. The p.e. spectra of these compounds $M(NR_2)_4$ [M = Ti, Zr, or Hf, with R = Me or Et and $V(NMe_2)_4$] are conveniently analysed in a similar manner as for the Group 4B amides; there is an additional section, (*d*), for $V(NMe_2)_4$. Section (*c*), as before, is disregarded. The M–N bonding m.o.s in section (*b*) should give two bands of symmetry E and B_2, but a single band was observed indicating little interaction with the N lone pairs and negligible spin–orbit interaction even for the compounds containing the heavy-metal atoms. This reflects the lower i.p.s of the transition-metal atomic orbitals contributing to the m.o. The i.p.s of this m.o. for the diethylamides are 0·6—0·9 eV lower than for the corresponding dimethylamides, as expected from the greater $+I$ effect of the ethyl compared with the methyl group. It is noteworthy that the i.p. of this m.o. is essentially independent of the nature of the metal atom. This was also noticed for the corresponding MC_4 m.o.s in MR_4 (M = Ti, Zr, or Hf, with R = Me_3CCH_2 or Me_3SiCH_2), and was attributed to a constancy of central-atom parameters from Ti to Hf.[1]

Turning now to section (*a*), four components were observed for each of the d^0 amides. Thus there is a complete loss of the degeneracy of the lone-pair orbitals which was a feature for Si and the d^{10} compounds. It follows that M–N free rotation is not occurring here. Thus the orbitals are split into the E, B_1, and A_1 components of the D_{2d} point group, and a further splitting of the E orbital was observed. This is either due to a geometric distortion of the molecules in their ground state, or a Jahn–Teller distortion in the excited state. By analogy with $C(NMe_2)_4$, the first two bands are assigned to the split m.o. of E symmetry and the successive bands to the m.o.s of B_1 and A_1 symmetry, respectively.

In the case of the vanadium amide, the band structure of the lone-pair orbitals is again different. Ionisation of the single unpaired d electron occurs at 6·19 eV. According to e.s.r. studies, this d electron occupies an orbital of B_1 symmetry.[15] The ground state of d^1 $V(NMe_2)_4$ is expected to be Jahn–Teller split, and this may either compensate for or multiply splittings in the excited state. In addition, triplet and singlet ionic states are possible. Orchard and his co-workers found

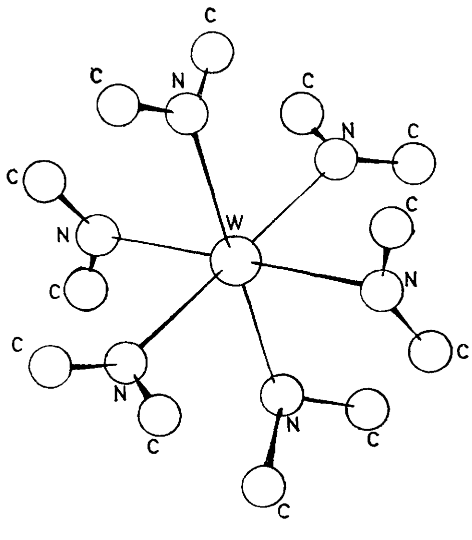

FIGURE 6 $M(NC_2)_6$ Framework in $W(NMe_2)_6$, illustrating T_h symmetry

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* 1 eV ≈ 1·60 × 10^{-19} J.

that the small exchange integrals between remote electrons and the central-metal *d* electron in VCl_4 gave a splitting so small as to be unobservable.[19] Apparently this is not the case for the amide. It appears that the lone-pair m.o. of B_1 symmetry is interacting strongly with the B_1 orbital from the *d* electron orbital, and the former thus appears at significantly higher i.p. (8·28 eV) than in the d^0 amides. The band was broad and had a shoulder on the high-energy side, perhaps indicative of singlet–triplet splitting in the ion. On the basis of this assignment, the positions of the *E* and A_1 lone-pair bands are, not unreasonably, substantially the same as for $Ti(NMe_2)_4$.

Tungsten Hexakis(dimethylamide).—The p.e. spectrum of $W(NMe_2)_6$ is shown in Figure 4. In the ' lone-pair region,' there were two bands, neither of which showed any splitting. At higher i.p. there was a split band containing two maxima (at 9·55 and 9·94 eV), due to ionisations from the metal–nitrogen bonding m.o.s. On the basis of T_h symmetry (assuming M–N restricted rotation), there are three orthogonal pairs of lone-pair orbitals (Figure 6). This gives rise to a T_u state (bonding to the tungsten *p* orbitals) and a T_g state (bonding to the metal *d* orbitals). The T_u state, however, is destabilised to some extent by one T_u bonding m.o. from the M–N bonds, and the net effect is to make it probably slightly antibonding. Conversely, the T_g orbital forms a bonding m.o. with the T_g orbitals from the tungsten *d* electrons. A schematic energy-level diagram is shown in Figure 7. The first band in the p.e. spectrum is therefore assigned to an essentially non-bonding lone-pair combination (T_u) at 6·74 eV, and the second band to a slightly bonding combination (T_g) at 7·92 eV. In the metal–nitrogen bonding region we observed the split band mentioned earlier, assigned to ionisation from the orbitals of *E* and T_u symmetry respectively at 9·94 and 9·55 eV. In support of this assignment, we note that (*i*) the band at 9·55 eV was the more intense, and (*ii*) the 5*d* orbitals (see Figure 7), which interact with the *E* combination, are likely to be more stabilising than the higher 5*p* orbitals, which interact with the T_u orbital.

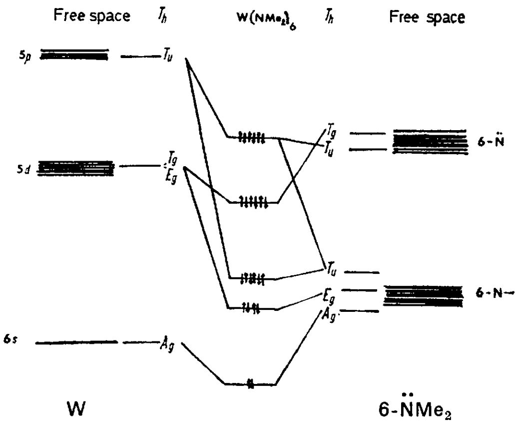

FIGURE 7 Schematic m.o. diagram for metal–ligand interaction in $W(NMe_2)_6$

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[19] P. A. Cox, S. Evans, A. Hammett, and A. F. Orchard, *Chem. Phys. Letters*, 1970, **7**, 414.