Bonding Studies of Transition–metal Complexes. Part III.[1] He(I) Photoelectron Spectra of Three-co-ordinate Homoleptic Bis(trimethylsilyl)-amides of Scandium, Titanium, Chromium, Iron, Gallium, and Indium †

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The He(I) photoelectron (p.e.) spectra of a number of three-co-ordinate metal amides $M[N(SiMe_3)_2]_3$ (M = Sc, Ti, Cr, Fe, Ga, or In) are presented. The spectrum of the d^0 scandium compound shows two bands at ionisation potential (i.p.) <9 eV, which are assigned to lone-pair orbitals. The spectra of the open-shell compounds are very similar, and it is concluded that bands corresponding to ionisation from the metal 3*d* orbitals lie at i.p. >9 eV, or are masked by bands due to ionisation from nitrogen lone-pair orbitals (>8.1 eV). This is attributed to a strong $-I$ effect of the ligand which, in contrast to the situation in corresponding dialkylamides such as $V(NMe_2)_4$, is not counterbalanced by a $\overset{\curvearrowright}{\ddot{\mathrm{N}}-\mathrm{M}}$ π interaction because of strong competing $\overset{\curvearrowright}{\ddot{\mathrm{N}}-\mathrm{Si}}$ $(p \longrightarrow d)$ π bonding.

RECENTLY a number of transition-metal complexes with the low and rare metal co-ordination number of three have been prepared.[2,3] The compounds $M(NR_2)_3$ and MR'_3,[4] where $R = SiMe_3$, $R' = (Me_3Si)_2CH$,[5] and M is a first-row transition element are, in principle, amenable to study by photoelectron (p.e.) spectroscopy. The former compounds are volatile, and may be sublimed without decomposition under high vacuum. Except for $Sc(NR_2)_3$, they all have rather high local symmetry for the $M(NSi_2)_3$ skeleton (D_3). Thus the crystal structure of $Fe[N(SiMe_3)_2]_3$ showed the FeN_3 group to be trigonal planar, whilst the ligand planes ($FeNSi_2$ units)

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† No reprints available.

[1] Part II, S. G. Gibbins, M. F. Lappert, J. B. Pedley, and G. J. Sharp, *J.C.S. Dalton*, 1975, 72.

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

[3] P. J. Davidson, M. F. Lappert, and R. Pearce, *Accounts Chem. Res.*, 1974, 209.

[4] E. C. Alyea, D. C. Bradley, and R. G. Copperthwaite, *J.C.S. Dalton*, 1972, 1580.

[5] G. K. Barker and M. F. Lappert, *J. Organometallic Chem.*, 1974, **76**, C45.

made a dihedral angle of 49° with the FeN_3 plane.[6] The scandium compound has a pyramidal (C_3) ScN_3 unit, although the ligands adopt a similar configuration to that found in the compounds of D_3 symmetry.[7]

We now report and discuss the p.e. spectra of NHR_2, $Sc(NR_2)_3$, $Ti(NR_2)_3$, $Cr(NR_2)_3$, and $Fe(NR_2)_3$, the metal compounds being d^0, d^1, d^3, and d^5, respectively, and the d^{10} $Ga(NR_2)_3$ and $In(NR_2)_3$. The results may be compared with those in Part II [1] on the tetrahedral or distorted-tetrahedral series $M(NMe_2)_4$ (M = Sn, Ti, Zr, or Hf) and $Cr(NEt_2)_4$, and octahedral $W(NMe_2)_6$, and in Part I [8] on some of the corresponding alkyls MR''_4.

EXPERIMENTAL

The samples of $M[N(SiMe_3)_2]_3$ (M = Sc, Ti, Cr, Fe, Ga, or In) were prepared by published procedures.[4,9] Product purity was checked by analysis, and i.r., ^1H n.m.r. (Sc), and mass spectra.

P.e. spectra were recorded on a modified PS16 He(I) photoelectron spectrometer, using the heated-inlet system.[1]

RESULTS

The spectra are shown in Figure 1, and the important ionisation potentials (i.p.s) are listed in the Table. For all the metal complexes, the low-i.p. region was scanned thoroughly with an expanded ordinate scale. No band was detected at lower i.p. than those shown in the Figure. The spectrum of $Ti[N(SiMe_3)_2]_3$ was difficult to obtain as the compound appears to undergo some decomposition at the temperature required for vaporisation.

DISCUSSION

First the free amine, hexamethyldisilazane, is considered (see ref. 10). The first band in the spectrum, at i.p. = 8.79 eV,* is clearly identified as corresponding to ionisation from the lone-pair orbital on the nitrogen atom. The proximity of this i.p. to the corresponding value for NMe_2H (8.8 eV) and NEt_2H (8.68 eV),[1] despite the greater $+I$ effect of the $SiMe_3$ groups, suggests that the lone-pair orbital may be stabilised by $\overset{\frown}{\ddot{\mathrm{N}}\text{–}\mathrm{Si}}$ $(p \longrightarrow d)$ π bonding. This will be discussed in more detail elsewhere in the context of two-co-ordinate main-group metal amides and alkyls.[11] The next two bands have been assigned to ionisation from the Si–C and Si–N bonding orbitals respectively.[10] While we substantially agree with this assignment, we draw attention to the fact that both of these bands are split in our spectrum.

In the scandium compound we observed two bands at low i.p. slightly overlapping, at 8.18 and 8.62 eV. The onset of a further band, at 9.45 eV, was also observed on the low-i.p. side of the bands at 10 eV and above. The latter bands correspond to ionisation from

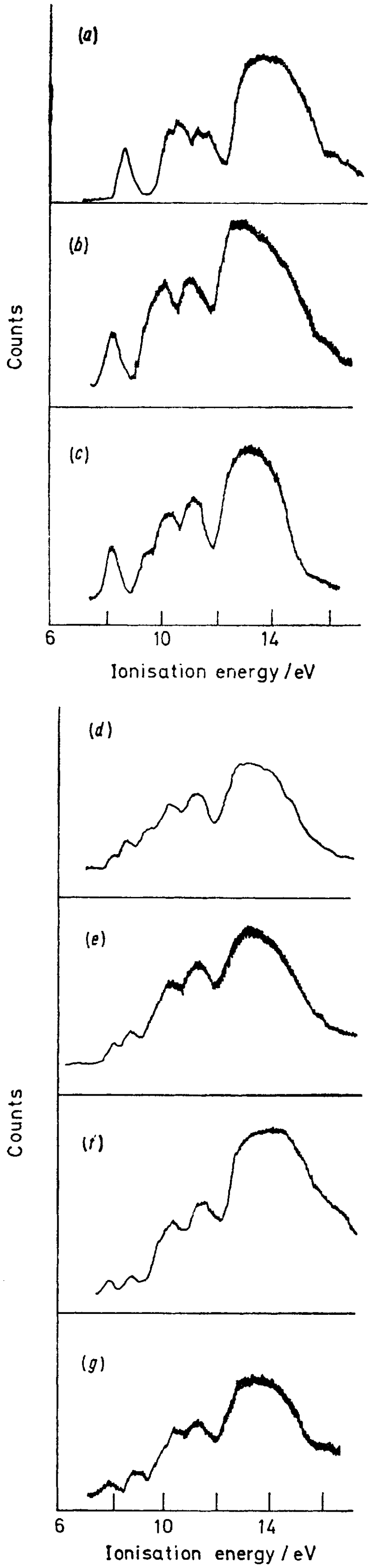

FIGURE 1 He(I) p.e. spectra of $NH(SiMe_3)_2$ (*a*) and $M[N(SiMe_3)_2]_3$ [M = Ga (*b*), In (*c*), Sc (*d*), Ti (*e*), Cr (*f*), or Fe (*g*)]

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* 1 eV $\approx 1.60 \times 10^{-19}$ J.

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[7] J. S. Ghotra, M. G. Hursthouse, and A. J. Welch, *J.C.S. Chem. Comm.*, 1973, 669.

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Vertical ionisation potentials (eV) of important bands

Compound	N lone-pair region			Ligand region				
$NH(SiMe_3)_2$		8.79		10.23	10.54	10.74	11.26	11.59
$Sc[N(SiMe_3)_2]_3$	8.18		8.62		10.09			10.98
$Ti[N(SiMe_3)_2]_3$	8.14		8.70		10.22			11.07
$Cr[N(SiMe_3)_2]_3$	8.07		8.76		10.16		11.04	11.21
$Fe[N(SiMe_3)_2]_3$	7.88		8.74		10.13		11.06	
$Ga[N(SiMe_3)_2]_3$		8.39			10.09			11.07
$In[N(SiMe_3)_2]_3$		8.30			10.22			11.11

ligand orbitals perturbed only slightly by spatial interactions. The band at 9.45 eV may correspond to the Sc–N bonding orbital of E symmetry. No corresponding band was observed in the spectra of the other compounds. This may be a reflection of the fact that scandium is the most electropositive of the metals concerned, and hence ionisation occurs from an orbital substantially localised on the nitrogen atom; consistent with this, the scandium compound is thus regarded as having high ionic character. The two low-i.p. bands are assigned to ionisation from the two nitrogen lone-pair orbitals of A and E symmetry. It is difficult to decide which of these is likely to be the higher in energy, since this is dependent on the knowledge of the dihedral angle between the ligand plane ($MNSi_2$) and the N_3 plane (or pyramid, for Sc). Thus (see Figure 2) if the lone pairs are perpendicular to the N_3 plane ($\theta = 0°$) the a_2'' orbital is more stable than e'', whereas if the lone pairs are in the plane ($\theta = 90°$) then e' is more stable than a_2'. The correct geometry ($\theta = 50°$) is intermediate between these extremes. [A similar situation has arisen before in connection with the p.e. spectra of $B(NMe_2)_3$,[12] and $P(NMe_2)_3$ and $PF_2(NMe_2)_3$.[13]] However, referring to the spectra (Figure 1), we note that the second band has a higher intensity than the first in all the complexes. Hence, we tentatively assign the bands to a_2 and e orbitals (in D_3 symmetry), in order of increasing i.p.

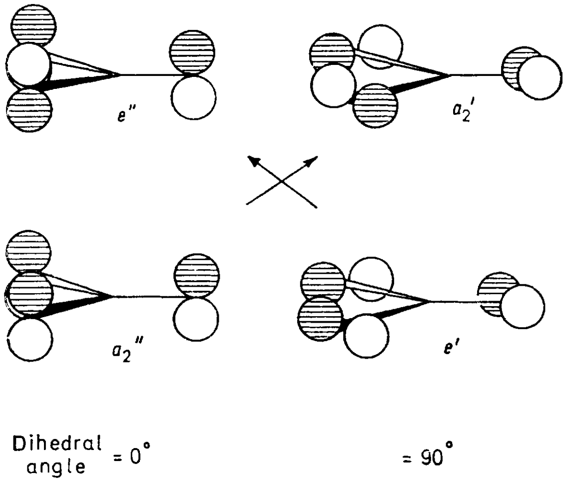

FIGURE 2 Variation of symmetry and energy of nitrogen a and e lone-pair orbitals with change in dihedral angle

Turning now to the open-shell d^1 $Ti(NR_2)_3$, d^3 $Cr(NR_2)_3$, and d^5 $Fe(NR_2)_3$, the p.e. spectra are clearly very similar to each other and to those of the scandium compound. The problem of interpretation of the u.v.–p.e. spectra of open-shell compounds has been discussed previously,[14] and as in that paper {dealing with the metallocenes $[M(\eta\text{-}C_5H_5)_2]$ (M = V, Cr, Mn, Co, or Ni)} we shall assume that Koopman's theorem has 'qualitative analogical significance' in a series of related compounds. Further, no bands were observed in our spectra which may be assigned to ionisation from the metal ion, and it seems less likely that orbitals predominantly on ligand atoms will be greatly perturbed. Only two bands were observed below 9.5 e.V. for these compounds, and these must again be associated with ionisation from the nitrogen lone-pair orbitals, although they may also overlap with d-orbital ionisations.

Two major effects influence the positions and splittings of the bands due to ionisation from nitrogen lone-pair orbitals. First (see above), the dihedral angle which the NSi_2 plane makes with the MN_3 plane affects the splitting. Secondly, the extent of interaction of the lone-pair orbitals depends on the M–N bond length, and increases as the M–N length decreases. In fact, the observed splittings are not related to bond length [Sc 0.44 (Sc–N 2.04); Ti 0.56 (Ti–N 1.93); Cr 0.71 (Cr–N 1.90); and Fe 0.86 eV (Fe–N 1.92 Å)]. We therefore conclude that within the series there are changes in dihedral angles. The structures of the complexes are not all known, so that the dependence of the a_2/e splitting of the dihedral angle must await further data.

The spectra of $Ga[N(SiMe_3)_2]_3$ and $In[N(SiMe_3)_2]_3$ each showed only one band at i.p. <9 eV, and this band was not split. This either indicates a weak interaction between the nitrogen lone-pair orbitals, possibly with free rotation about the metal–nitrogen bond, or accidental degeneracy of the orbitals of A and E symmetry due to the prevailing dihedral angle between the NSi_2 groups and the MN_3 plane. It is noteworthy that this situation (*i.e.* nitrogen lone pairs not split for complexes of B group elements) exactly parallels the results obtained on the tetrakis(dialkylamides) of Group 4B elements.[1] A further point of interest concerning the spectra of the gallium and indium compounds is that whereas there was no low-i.p. shoulder on the band with vertical i.p. 10.12 eV for the gallium compound, there was a shoulder (at 9.13 eV) on the corresponding band for the indium compound. This is assigned to the In–N bonding orbital of E symmetry. Since this orbital is likely to be substantially localised on the nitrogen atoms, the appearance of the band for the indium, but

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[12] H. Bock and W. Fuss, *Chem. Ber.*, 1971, **104**, 1687; G. H. King, S. S. Krishnamurthy, M. F. Lappert, and J. B. Pedley, *Faraday Discuss. Chem. Soc.*, 1972, **54**, 70.

[13] A. H. Cowley, M. J. S. Dewar, D. W. Goodman, and J. R. Schweiger, *J. Amer. Chem. Soc.*, 1973, **95**, 6506; M. F. Lappert, J. B. Pedley, O. Stelzer, O. Unger, and B. T. Wilkins, *J.C.S. Dalton*, 1975, 1207.

[14] S. Evans, M. L. H. Green, B. Jewitt, G. H. King, and A. F. Orchard, *J.C.S. Faraday II*, 1974, 356.

not for the gallium, is probably due to the greater electron-releasing ability of the heavier central atom. This also supports the assignment of a similar shoulder in the scandium compound to the Sc–N orbital of E symmetry, since scandium is the most electropositive of the transition metals studied here.

The most notable feature of the p.e. spectra of the d^1–d^5 amides is that no bands were observed below 9 eV which may be identified with ionisation from d orbitals, even for the high-spin [15] d^5 iron(III) compound, although the bands, if weak, may be masked by the ionisation from the nitrogen lone-pair orbitals. This requires some comment, since in a previous paper [1] we observed that the i.p. of the d electron in $V(NMe_2)_4$ is at the low value of 6.2 eV. It follows that the influence of the NMe_2^- and $N(SiMe_3)_2^-$ ligands on an attached metal is substantially different. Nitrogen is a highly electronegative atom, and, adjacent to the central metal, exerts a strong electron-withdrawing effect. The low first i.p. of the $V(NMe_2)_4$ compound is accounted for by counterbalancing $\overset{\curvearrowright}{\ddot{\mathrm{N}}\text{–}\mathrm{M}}$ π interaction between the nitrogen lone pairs and the central d orbitals. Evidence for this proposition comes from X-ray data [2] on the trigonal disposition of valencies at nitrogen in metal dialkylamides as required by such $\overset{\curvearrowright}{\ddot{\mathrm{N}}\text{–}\mathrm{M}}$ (p–d) π bonding. In the disilylamide compounds, however, we suggest that the N–M π interaction is suppressed. This we attribute to the competing strong nitrogen lone-pair orbital interaction with the vacant $3d$ orbitals on the silicon atoms. The consequences of this are two-fold. First, the central atom d electrons are subjected principally to a strong electron-withdrawing effect, so that the d orbitals are found at i.p. $\geqslant 8$ eV, and, secondly, the nitrogen lone-pair orbitals are stabilised by their interaction with the vacant Si d orbitals. Accordingly, whereas in $Ti(NMe_2)_4$, for example, the average nitrogen lone-pair i.p. is at *ca.* 7.6 eV, in the disilylamides the weighted average i.p. (allowing for the degeneracy of the e orbitals) is probably nearer to 8.3 eV. Recent crystal-structure data on $M[N(SiMe_3)_2]_3$ ($M =$ Al, Ga, or In) give M–N bond lengths consistent with a single bond,[16] in accord with conclusions drawn here from p.e. work.

In drawing these conclusions we assume that the electronic structures of the d^n compounds are such that there are partially filled orbitals higher in i.p. than some of the totally occupied orbitals and this is especially surprising for the d^1 compound where there can be no compensating exchange stabilisation. (However, the mean d-orbital atomic i.p. of titanium is 9.94 eV.) [17] Orchard and his co-workers [18] have similarly interpreted the p.e. spectra of some transition-metal tris(β-ketonates) and this feature may prove rather general also for other transition-metal complexes. It might have been expected that the d-orbital ionisations would be observed as sharp peaks at higher i.p., as with the inner-orbital ionisations in mercury compounds.[19] However, as noted above, the disilylamides have substantial polar character. It has been suggested that an orbital predominantly localised on the central atom in a compound of high ionicity will, on ionisation, give rise to a broad band in the p.e. spectrum.[20] The cause of this is the change in bond length occurring on ionisation. Removal of a central-atom electron causes shortening of the bond length so that an orbital localised on the central atom appears to behave as an antibonding orbital. The p.e. band produced will thus be broad, despite the formal non-bonding nature of the electron in the molecule.

It would be interesting to develop a detailed molecular-orbital description of these open-shell disilylamides which is consistent not only with the present results, but also with those based on electronic, e.s.r., or Mössbauer spectra.[15] The electronic absorption spectra were interpreted [15] in terms of simple crystal-field theory, *i.e.* perturbation of d orbitals by a trigonal electric field in D_{3h} symmetry. This provides energies of excited states relative to electronic ground states of the M^{3+} ions, but provides no information about energies of ligand orbitals. However, from the electronic spectra of the d^5 $Fe(NR_2)_3$ system it is apparent that two of the d electrons are 19 350 cm^{-1} higher in energy than a third which in turn is separated by 1 900 cm^{-1} from the lowest-energy d electrons. In the d^3 $Cr(NR_2)_3$ system there should be a 3 000 cm^{-1} separation between the two occupied levels. These conclusions were supported by e.s.r., and for Fe^{3+}, by Mössbauer, data.[15] The overall picture, including p.e. spectra, therefore is that $d \longrightarrow d$ optical transitions occur independently of filled, energetically more accessible, ligand orbitals. A possible explanation for this apparent paradox is that metal d-electron and ligand orbitals are essentially uncoupled. There is precedent for this in metalloporphins, wherein ligand electrons are substantially delocalised; [21] alternatively, Koopman's theorem is invalid for these molecules. First i.p.s of some tris(β-ketonate)metal(III) complexes, including pentane-2,4-dionates or hexafluoro-analogues of Al^{3+}, Cr^{3+}, and Fe^{3+}, were likewise found to be similar to those of the hydrido-ligand pentane-2,4-dione (8.87 eV) or facH (10.68 eV).[18,22]

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