Ligand-field Traces in Three- and Five-co-ordinated Transition-metal(III) Complexes

Neil D. Fenton and Malcolm Gerloch *
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

Ligand-field analyses of published '*d–d*' transition energies, paramagnetic susceptibilities, zero-field splittings, and *g* values in two series of transition-metal(III) complexes have been performed within the cellular ligand-field (c.l.f.) approach. One series comprises the three-co-ordinated tris[bis(trimethylsilyl)amido] complexes of Ti^{III}, V^{III}, Cr^{III}, and Fe^{III}. The other involves trigonal-bipyramidal complexes [$MX_3(NMe_3)_2$] (X = Cl or Br for M = Ti^{III} or V^{III}; X = Cl for Cr^{III}). The silylamido groups are demonstrated to act as σ donors and strong π donors throughout the series. The sum of all c.l.f. parameters in each complex, called the ligand-field trace, Σ, is likely to be constant throughout that series, with a value of *ca.* 31 500 cm^{-1}. The trace is probably also constant throughout the five-co-ordinate set of compounds, taking a value between 50 000 and 61 000 cm^{-1}. Detailed variations of all ligand-field parameters throughout each series are shown to accord well with general principles of chemical bonding.

Ligand-field theory (l.f.t.) is properly applied to the reproduction and interpretation of those spectral and magnetic properties that may be considered as consequences of the primary bonding in transition-metal complexes. It is to be viewed as a projection of the many-electron problem onto a *d* (*f*) orbital basis.[1–4] An especially useful form of ligand-field theory, in terms of the chemical transparency of its parameters, is one which exploits superposition over local regions of space (cells) usually associated with individual ligands, that we call the cellular ligand-field (c.l.f.) model.[5] This has the same phenomenological form and parameter names as does the angular overlap model (a.o.m.) but lies entirely within the definable ligand-field regime and does not admit quantities that belong only outside of l.f.t. One attribute of the a.o.m. that is deceptively and unfortunately attractive is the idea that e_λ parameters are (even approximately) transferable between systems.[6] Empirically, however, freely varied e_λ parameters within a ligand-field analysis of ligand-field properties, spectra and magnetism take values which can change within chemical series.[3] Such changes, when they occur, can be very large but in all cases are readily comprehensible by reference to trends that will have occurred in the primary bonding. Ligand-field parameters are thus to be seen as probes into, or reflections of, the underlying electron distribution. Nevertheless, within the proper ligand-field formalism, one feature has emerged[7,8] empirically to have some degree of transferability between systems. It is the sum, Σ, of the values of all locally diagonal e_λ parameters in a complex. That sum is analytically equal to the trace of the global ligand-field matrix. Nearly all determinations of its value to date have been obtained from ligand-field analyses of the spectra and magnetism of metal(II) complexes on the right-hand side of the first transition series.[7,8] The trace, Σ, takes an essentially constant value irrespective of co-ordination number and geometry, or of metal(II). It does vary with respect to the ligand, taking values of 28 000, 22 000, 21 000, and 15 000 cm^{-1} for imine, chloro, amine, and phosphines, respectively: the last figure is rather tentative at this stage, being based on rather few certain analyses. That the trace of a c.l.f. matrix should be non-zero has been demonstrated theoretically by Woolley.[9] The significance of its magnitude is currently being studied in our laboratory. It is clear that a wider sampling of trace values across the transition series is required. In the tris(ethylenediamine)chromium(III) ion, we have determined[10] a value for Σ of *ca.* 46 000 cm^{-1}, which illustrates the kind of variation that can be associated with the change in formal oxidation state. The present paper describes an attempt to enlarge our experience of the ligand-field trace for metal(III) complexes.

We have considered two different, though structurally somewhat related, series. The first comprises three-co-ordinate complexes of the bis(trimethylsilyl)amido anion with Ti^{III}, V^{III}, Cr^{III}, and Fe^{III}. This series has been extensively studied by Bradley and co-workers[11–13] from synthetic, structural, and electronic viewpoints and their work has been put into the wider context of three-co-ordination in a review.[14] Hursthouse and co-workers[15,16] have reported crystallographic analyses for each member of the series; they are very closely isostructural. Electron-spin resonance studies[13] have been carried out on the titanium, chromium, and iron compounds and the mean paramagnetic susceptibilities and electronic spectra have been recorded[12] for each member of the series. All these electronic properties have been rationalized[12] within a crystal-field approach using an idealized D_{3h} symmetry. The possible inadequacy of this latter simplification was emphasised by Eller *et al.*[14] and such is shown to be the case in the present study.

The second series considered here involves the five-co-ordinate, near trigonal-bipyramidal, complexes [MX_3L_2] [M = Ti^{III}, V^{III}, or Cr^{III}; X = Cl or Br (Cl only for M = Cr^{III}); L = NMe_3]. The syntheses and electronic spectra of these compounds have been reported by Fowles and co-workers[17–19] and crystallographic structural analyses[20,21] have been completed for three members of the series.

We report here on the results of comprehensive ligand-field analyses on all nine complexes within the modern c.l.f. approach.

Results

Geometry, Parameters, and Bases.—The co-ordination in the three-co-ordinate series is shown in Figure 1. The low co-ordination number is considered[14] to arise from the bulk of the bis(trimethylsilyl)amido groups which pack around the central metal in a 'propeller' arrangement. The metal atom lies in each NSi_2 plane and nearly within the plane of the three donor nitrogen atoms. Some relevant structural parameters are summarized in Table 1, including the dihedral angle φ between the NSi_2 and N_3 planes. The planarity of the $MNSi_2$ co-ordination and the M–N–Si angles both indicate trigonal hybridization for

Table 1. Structural parameters for $[M\{N(SiMe_3)_2\}_3]$ complexes

Metal(III)	Titanium[16]	Vanadium[16]	Chromium[16]	Iron[15]
M-N/Å	1.93	1.91	1.90	1.92
M-N-Si/°	120	120	119	119
φ*/°	50	51	53	49

* Dihedral angle between NSi_2 and N_3 planes, see Figure 1.

Table 2. Structural parameters for $[MX_3(NMe_3)_2]$ species, see Figure 2

Complex	$[TiBr_3(NMe_3)_2]$	$[VCl_3(NMe_3)_2]$	$[CrCl_3(NMe_3)_2]$
M-N(1)/Å	2.27	2.20	2.16
M-N(2)/Å	2.36	2.23	2.14
M-X(1)/Å	2.44	2.24	2.22
M-X(2)/Å	2.40	2.34	2.25
N(1)-M-N(2)/°	179	179	179
X(1)-M-X(2)/°	121	121	124
X(1)-M-X(1')/°	118	118	111

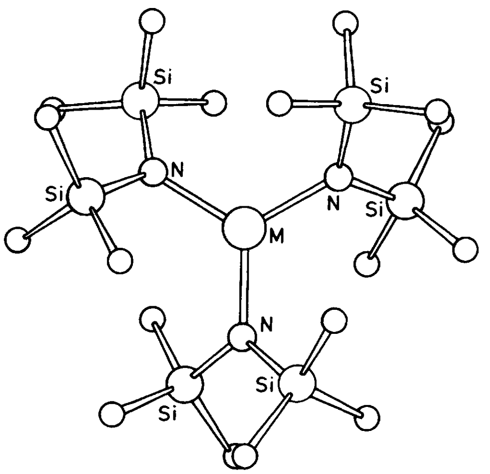

Figure 1. Three-fold co-ordination[14] in bis(trimethylsilyl)amido complexes of M^{III} (M = Ti, V, Cr, or Fe)

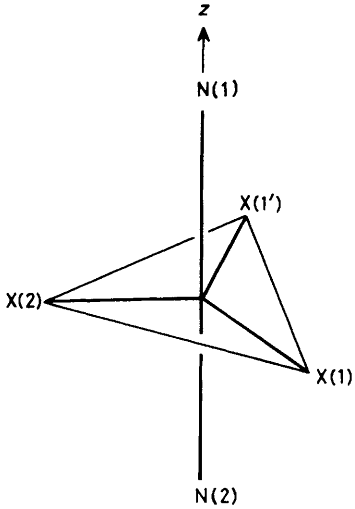

Figure 2. Labelling in trigonal-bipyramidal co-ordination: see Table 2

the donor nitrogens. If no π interaction between metal and ligand is evident, the chromophore symmetry approaches D_{3h} very closely: otherwise the propeller packing requires a D_3 description. Estimates[14] of the metal–nitrogen bond lengths for σ bonding only suggest[14] that those listed in Table 1 are between 0.03 and 0.05 Å shorter due to π interaction.

The present c.l.f. parameter set comprises $e_\sigma(N)$ and $e_{\pi\perp}(N)$ for the metal–ligand interactions, the latter defined as perpendicular to each local $MNSi_2$ plane, and e_σ(void) associated with each co-ordination void, above and below the N_3 plane. A large, negative value for this ligand-field contribution is expected by comparison with extensive work on other planar, and related, systems.[22] In addition to these ligand-field parameters, we include the one-electron spin–orbit coupling coefficient ζ and, where appropriate, the Racah interelectron repulsion parameters B and C. As usual, the free-ion d^n basis, or mostly those terms of maximum spin multiplicity, have been diagonalized under the simultaneous perturbations of the Coulomb operator, the ligand field and spin–orbit coupling. Paramagnetic susceptibilities and e.s.r. g values were calculated by subsequent perturbation theory using the magnetic moment operator $\mu_\alpha = kl_\alpha + 2s_\alpha$; $\alpha = x, y, z$ where k is Stevens' orbital reduction factor.

The co-ordination geometry of the five-co-ordinate species is summarized in Figure 2 and Table 2. Departures from exact D_{3h} symmetry in these chromophores arise partly from the unequal X(1)–M–X(2) angles [more for the chromium(III) complex] but mostly from the inequality of the axial metal–amine bond lengths.

The ligand field was parameterized with $e_\sigma(N)$ for the mean of the diametrically opposed amine ligations, together with $e_\sigma(X)$ and $e_\pi(X)$ for σ and π interactions with the equatorial ligands. Other parameters and bases were included, as appropriate, as for the three-co-ordinate series.

All computations were performed using the CAMMAG2 suite of programs[23] for ligand-field analysis, together with the detailed co-ordination geometries established by structural analysis.

The Three-co-ordinate Series.—Analysis for the titanium(III) *complex*. Three spectral absorptions are reported[12] for this complex, at 4 800, 17 400, and 28 600 cm^{-1}. In D_3 symmetry only two are expected, corresponding to the transitions $A_1 \longrightarrow E, E$. As the band at 28 600 cm^{-1} is much more intense than the others, it has been proposed[12] that this represents a charge-

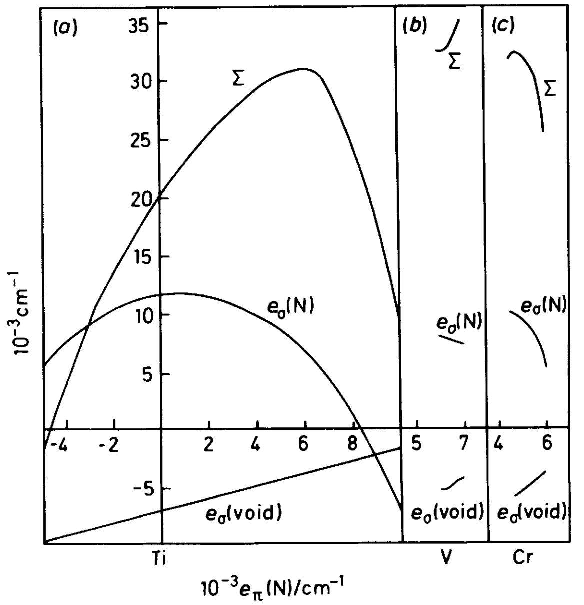

Figure 3. Correlations between c.l.f. parameters affording good reproduction of all experimental data in silylamido complexes of (*a*) titanium(III), (*b*) vanadium(III), and (*c*) chromium(III). The corresponding values of the ligand-field trace, Σ, are included. Acceptable fitting regions are much more closely bounded for vanadium and chromium than for titanium

transfer transition: alternatively, the band at 4 800 cm^{-1} could be assigned to a vibrational overtone. Wide variations of all three c.l.f. parameters yield fits for either assignment. The ambiguity is removed, however, by consideration of the reported[13] e.s.r. g values, $g_\parallel = 1.993$, $g_\perp = 1.869$. In D_{3h} symmetry, the expected orbital ordering is $d_{z^2} < d_{xz,yz} < d_{xy,x^2-y^2}$. In D_3 symmetry when account of π interactions perpendicular to the NSi$_2$ planes is taken, orbitals with these majority characters are also likely to order in this fashion. Departures from $g = 2$ will occur only *via* the shift operators $l\pm$ and so, with $\zeta_0 = 154$ cm^{-1} (the free-ion value) for Ti^{3+}, a correct reproduction of $g_\perp$ must require only a modest energy separation of d_{z^2} and $d_{xz,yz}$. All this is confirmed by the full ligand-field calculations which select the two lower spectral bands as *d*–*d* transitions. The observed transition energies are reproduced by a wide selection of ligand-field parameter values, however, as is to be expected in this high molecular symmetry with three c.l.f. variables. The nature of the parameter correlation affording good spectral fit is shown in Figure 3(*a*). For each parameter selection, the g values are quantitatively reproduced for ζ and k values taken such that $k\zeta = 125$ cm^{-1}. Further selection of a 'best' c.l.f. parameter set is made later by comparison with results from the analyses of the corresponding vanadium and chromium complexes now described.

Analysis for the vanadium(III) *complex.* The spectrum of this complex in cyclopentane solution reveals transitions at *ca.* 12 000, 15 900, 19 200, and 24 700 cm^{-1}. The mean magnetic moment at room temperature confirms a spin-triplet ground term. Wide variations of all e_λ parameters: from $-5\,000$ to 13 000 cm^{-1} for e_σ(N), 0 to $-10\,000$ cm^{-1} for e_σ(void), and 0 to 10 000 cm^{-1} for $e_{\pi\perp}$(N) were considered within the full spin-triplet basis. The band observed at 24 700 cm^{-1} was assigned either to a charge-transfer band alone or to include a *d*–*d* transition (which was ultimately selected). At the same time, the lowest-energy band observed was recognized to determine a transition no more exactly than in the range 10 500—13 000 cm^{-1}. A single, quite small, region of parameter space was found to reproduce experiment satisfactorily, the correlations within this region being shown in Figure 3(*b*). All portions of Figure 3 are drawn on the same scale, so that the much better determined fit for the vanadium complex relative to the titanium is immediately apparent.

Analysis for the chromium(III) *complex.* The diffuse reflectance spectrum of the chromium(III) compound has been reported[12] to show two bands at 15 000 and 12 000 cm^{-1} together with a very weak feature at 8 400 cm^{-1}. Fitting these bands within the spin-quartet basis of d^3 by variation of e_σ(N), $e_{\pi\perp}$(N), e_σ(void), and B proved, as expected, to be hopelessly underdetermined. A reasonably unique parameter set was obtained, however, after simultaneous analysis of the e.s.r. spectrum.[13] While g values were not especially well determined in this system, the reported magnitudes of *ca.* 2 and 4 are wholly compatible with resonances expected from an axial system suffering zero-field splitting. That splitting, however, has been well determined[13] as 3.7 cm^{-1} ($D = -1.85$ cm^{-1}), the negative sign indicating that the $M_S = \pm\frac{3}{2}$ state lies lower in energy than the $M_S = \pm\frac{1}{2}$ state, having been established by depopulation experiments. Accordingly, our criteria for c.l.f. analysis have been the requirement that the *d*–*d* bands at 15 000 and 12 000 cm^{-1} be reproduced together with a negative zero-field splitting (z.f.s.) with a magnitude greater than or equal to 3.7 cm^{-1} when ζ is held fixed at ζ_0 (= 273 cm^{-1}). As the z.f.s. is effectively proportional to ζ, a calculated value greater than 3.7 cm^{-1} can be 'corrected' by reduction in ζ. Even these conditions left a large ambiguity in the ligand-field parameter set but when supplemented with the requirements that the trace Σ be positive, that e_σ(N) be positive, and e_σ(void) be negative (although this latter mostly occurred automatically following the other criteria), a greatly restricted fitting region was obtained. It is characterized by $e_{\pi\perp}$(N) taking a positive value. Figure 3(*c*) illustrates the covariation of e_λ within the bounds $4\,600 < e_{\pi\perp}(\text{N}) < 6\,000$ cm^{-1}. The ligand-field trace, Σ, lies within the range 25 700—32 500 cm^{-1}. We note also that the weak spectral feature at 8 400 cm^{-1}, which was not included in the set of fitting criteria, *is* reproduced by this parameter set.

Analysis for the iron(III) *complex.* The electronic spectrum for the iron analogue shows[12] two broad bands at 16 000 and 20 000 cm^{-1} together with several, much more intense, absorptions at higher energy. Mean magnetic susceptibility[12] and Mössbauer[24] measurements establish the high-spin ground state in this system. Once again, e.s.r. work[13] has determined g values as *ca.* 2 and 6, values which are compatible with an $S = \frac{5}{2}$ ground state suffering zero-field splitting in an axial environment. The magnitude of the z.f.s parameter has been measured as $D = -1.0$ cm^{-1}, the negative sign corresponding to the $M_S = \pm\frac{5}{2}$ Kramers' doublet lying lowest, having been established once more from depopulation experiments. Calculations have been performed within the basis of the ground spin-sextet plus all excited spin-quartet states. The poorly-featured electronic spectrum has prevented any useful discrimination of ligand-field parameter values and we are able to make only one certain observation. It is that, with the presumptions of a positive ligand-field trace, positive values for e_σ(N), and a negative value for e_σ(void), the metal–silylamido π interaction is again characterized by *positive* $e_{\pi\perp}$ values.

The Five-co-ordinate Species.—The titanium(III) *complexes.* The co-ordination geometry of all complexes in this series closely approaches D_{3h} symmetry. Small distortions are evident from the structural data given in Table 2 and are somewhat greater with respect to three-fold symmetry for the chromium compound than for the titanium or vanadium ones. Both [TiCl$_3$(NMe$_3$)$_2$] and [TiBr$_3$(NMe$_3$)$_2$] display only two absorption bands in their electronic spectra[19] as is to be expected in trigonal-bipyramidal geometry. These are assigned

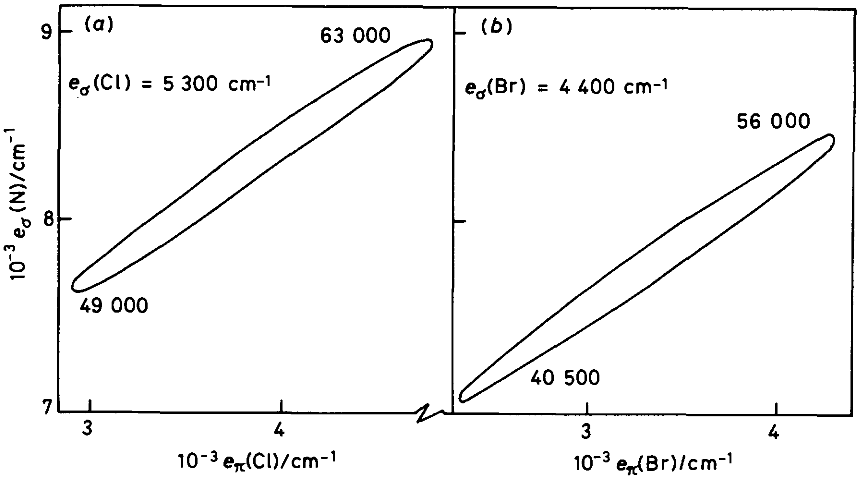

Figure 4. Acceptable c.l.f. parameter values to reproduce all experimental data in (*a*) $[TiCl_3(NMe_3)_2]$ and (*b*) $[TiBr_3(NMe_3)_2]$. Values of Σ at the limits of each area are also given

as $d_{xz,yz} \longrightarrow d_{xy,x^2-y^2}$ and $\longrightarrow d_{z^2}$ for the lower and higher energy transitions, respectively. The c.l.f. model is parameterized with e_σ(N), e_σ(X), e_π(X) (X = Cl or Br) and in exact D_{3h} symmetry we therefore expect an unbounded correlation between fitting parameters. In practice, that correlation may not be infinitely long in view of the small departures from exact D_{3h} symmetry. This is borne out empirically with respect to e_σ(N) and e_π(X). All fits to experiment are characterized, however, by an essentially unique value for e_σ(X). This element of determinacy arises from the fact that π interactions with the equatorial halogens give rise to equal energy shifts to both (*xz*, *yz*) and (*xy*, $x^2 - y^2$) orbital pairs, as may be checked by reference to Table 8.3 of ref. 25. For the chloro compound, e_σ(Cl) is thus determined as 5 300 cm^{-1} and for the bromo, e_σ(Br) = 4 400 cm^{-1}. The remaining indeterminacy in e_σ(N) and e_π(N) and e_π(X) parameters, together with the derived trace values, is shown in Figure 4. Mean paramagnetic susceptibilities have been reported[26,27] throughout the temperature range 90—300 K for both complexes and are reproduced from the constant orbital energies for the product $k\zeta$ equal to *ca.* 125 cm^{-1} in each case.

The vanadium(III) *complexes.* The diffuse reflectance spectrum[19] of $[VCl_3(NMe_3)_2]$ is characterized by three well resolved absorptions at 4 900, 7 100, and 20 100 cm^{-1} together with a complex region between 11 000 and 16 000 cm^{-1} in which are found one reasonably clear maximum at 12 500 cm^{-1} and three shoulders at *ca.* 11 600, 15 000, and 15 500 cm^{-1}. Within the spin-triplet basis of the d^2 configuration, *no* combination of values for the parameters e_σ(N), e_σ(Cl), e_π(Cl), *B*, and ζ affords reproduction of the spectrum if assigned as seven spin-allowed transitions. We have therefore considered that some or all of the features in the energy range 11 000—16 000 cm^{-1} are to be attributed to spin-forbidden transitions. As is well known, discriminations between spin-allowed and spin-forbidden transitions are especially unreliable for diffuse-reflectance spectra. Three assignments have been explored. In assignment A, only the band at 12 500 cm^{-1} is taken as spin-allowed; in assignment B, only that at 15 600 cm^{-1} is presumed spin-allowed, and in assignment C, all four features in the range 11 000—16 000 cm^{-1} are assigned as spin-forbidden. As for the titanium complexes, essentially unique values for e_σ(Cl) were determined for each assignment while e_σ(N) and e_π(Cl) values remained widely undetermined but correlated. Final refinements of all three analyses were made by seeking reproduction of both spin-allowed and spin-forbidden bands within the complete d^2 basis. Best fits are obtained as shown below.

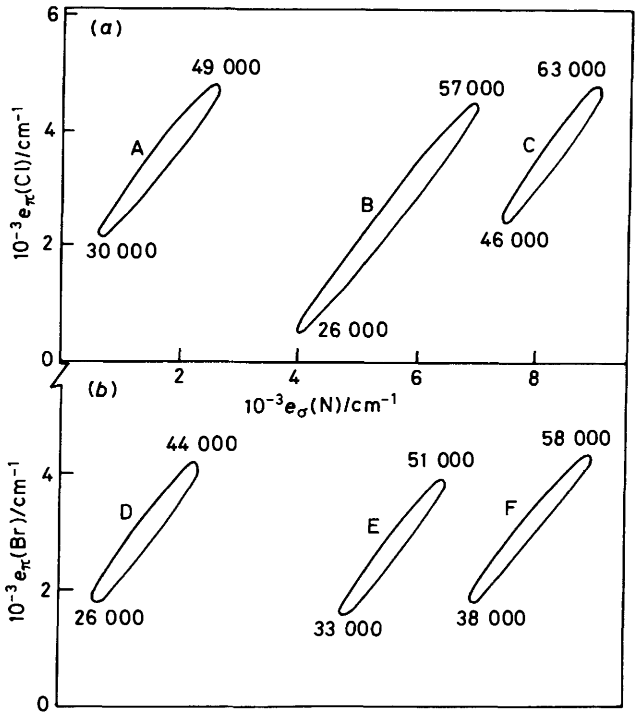

Figure 5. Acceptable c.l.f. parameter values to reproduce all experimental data in (*a*) $[VCl_3(NMe_3)_2]$ and (*b*) $[VBr_3(NMe_3)_2]$. Discrete areas refer to different spectral assignments as labelled, see text. Values of Σ at the limits of each area are included

Assignment A: e_σ(Cl) = 5 000 cm^{-1} with e_σ(N) = 0.753e_π(Cl) − 940 cm^{-1} for e_σ(N) in the range 0—2 600 cm^{-1}

Assignment B: e_σ(Cl) = 5 150 cm^{-1} with e_σ(N) = 0.751 e_π(Cl) + 3 600 cm^{-1} for e_σ(N) in the range 4 000—7 000 cm^{-1}

Assignment C: e_σ(Cl) = 5 300 cm^{-1} with e_σ(N) = 0.755 e_π(Cl) + 5 475 cm^{-1} for e_σ(N) in the range 8 000—8 600 cm^{-1}

These correlations are also illustrated in Figure 5 in which are included limiting values of the ligand-field trace, Σ. For each assignment, the c.l.f. parameters are determined by the clearer features of the spectrum: estimates for the Racah *C* parameter are less well established by the unresolved nature of the spin-forbidden transitions.

The situation for the bromo analogue is closely similar. Bands are reported[19] in the diffuse reflectance spectrum at 4 200, 6 100, 10 800, 13 000, 14 500, and 18 700 cm^{-1}. A detailed *X*-ray structure has not been reported for this complex but isomorphism with its chloro analogue has been demonstrated.[19] We assume it is also isostructural. For similar reasons, we have considered three assignments. In assignment D, bands observed at 10 800 and 14 500 cm^{-1} are deemed to be spin-forbidden; in assignment E, those at 10 800 and 13 000 cm^{-1} are so assigned; and in assignment F, all three features lying between 10 000 and 15 000 cm^{-1} are presumed to be spin-forbidden transitions. Analyses for each assignment followed the same procedures as for the chloro complex, first within a spin-triplet basis and then within the 45 functions of d^2. The best reproductions of experiment were obtained as shown below.

Assignment D: e_σ(Br) = 4 700 cm^{-1} with e_σ(N) = 0.741 e_π(Br) − 830 cm^{-1} for e_σ(N) in the range 500—2 300 cm^{-1}

Assignment E: e_σ(Br) = 4 700 cm^{-1} with e_σ(N) = 0.754 e_π(Br) + 3 490 cm^{-1} for e_σ(N) in the range 4 700—6 500 cm^{-1}

Assignment F: e_σ(Br) = 4 500 cm^{-1} with e_σ(N) = 0.748 e_π(Br) + 5 620 cm^{-1} for e_σ(N) in the range 6 600—9 200 cm^{-1}

Again, these correlations, together with appropriate Σ values are shown in Figure 5.

Powder susceptibilities for both complexes have been reported[18] at room temperature only. With *k* and ζ values related by the product *k*ζ = 150 cm^{-1} in each case, the observed values can be reproduced for all otherwise acceptable choices of ligand-field and interelectron repulsion parameters. The mean moments thus serve merely to confirm the spin-triplet nature of the ground states.

The chromium(III) *complex*. The electronic spectrum of [$CrCl_3(NMe_3)_2$] has been recorded[17] in benzene solution and also as a solid by diffuse reflectance. The two spectra are closely similar, showing two strong peaks at low energy (10 100 and 17 600 cm^{-1}) that are attributed[18] to spin-allowed *d–d* transitions together with two far weaker features at 13 000 and 23 200 cm^{-1}, presumed to be spin-forbidden transitions. A further, very intense, absorption at 30 000 cm^{-1}, like others at even higher energy is assigned as non *d–d*, although we consider the possibility of *d–d* transitions lying within the envelope of this strong absorption. Wide variations of e_σ(Cl), e_π(Cl), e_σ(N), and *B* were examined in a c.l.f. analysis within the spin-quartet terms of d^3: no restrictions were placed upon e_π(Cl) but e_σ values were constrained to be positive and *B* was varied within the range 500 < *B* < 1 030 cm^{-1} (B_0 = 1 030 cm^{-1}). As for the titanium and vanadium complexes, a virtually unique value for e_σ(Cl) is required to reproduce the observed spectral features but correlated values of the remaining variables lie within wide ranges. In all cases, calculated spin-allowed bands occur around 10 000, 18 000, and 30 000 cm^{-1}. Considerable narrowing of the correlated region of good fit is obtained, however, when the basis is enlarged to the complete 120-fold d^3 manifold and reproduction of the spin-forbidden bands is also attempted. The value of e_σ(Cl) is confirmed as 4 500 cm^{-1} and the remaining c.l.f. parameters are related by e_σ(N) = 0.75e_π(Cl) + 7 000 cm^{-1}, with e_π(Cl) lying in the range 1 900—4 500 cm^{-1}. As before these conclusions are insignificantly affected by variation of the spin-orbit coupling coefficient.

Powder magnetic susceptibilities have been measured[26] for this complex over the temperature range 90—300 K. Their reproduction requires a value for the product *k*ζ of only 105 cm^{-1} and is valuable in the present analysis in that the only region of parameter space that is unacceptable with respect to reproduction of the magnetism lies in the middle of that region determined by the spectral analysis. Simultaneous reproduction of spectral and magnetic properties within the full basis of d^3 thus selects two discrete small regions of parameter space designated 'high trace' and 'low trace', corresponding to their associated Σ values being 61 300 and 42 400 cm^{-1}, respectively.

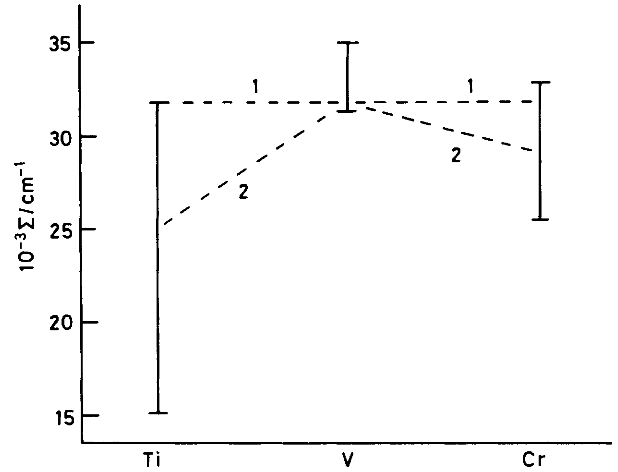

Figure 6. Bounds of possible ligand-field trace values for the silylamido complexes; see also Figure 3. Broken lines 1 and 2 identify trends discussed in the text

Discussion and Conclusions

From the outset, it was obvious that complete definitions of the ligand-field parameters could not be expected from analyses of these high-symmetry species. While the widths of the enclosed fitting regions shown in Figure 4 probably reflect the quality of the reported spectra (which were, in any case, very difficult to obtain in the case of the three-co-ordinate species), the extents of those regions, as represented for example by Figure 3, derive mostly from the high molecular symmetry. The measurements of zero-field splittings and of their signs by depopulation work were very useful for the analyses of the silylamido complexes. In the following discussion, we emphasise the division between those conclusions which are certain and those which are merely probable. In all cases, from both three- and five-co-ordinate series, good reproduction of all experimental data has been achieved and is detailed later in Tables 4 and 6.

We begin with the three-co-ordinate species. The silylamido ligands have been shown unequivocally to act as π *donors* towards V^{III}, Cr^{III}, and Fe^{III}. We confidently presume they act similarly towards Ti^{III}. Ranges of acceptable ligand-field parameters have been determined for all but the iron complex. As Figure 3 shows, those ranges are large for the titanium system but reasonably small for the vanadium and chromium ones. In Figure 6 are summarized the values of the ligand-field trace, Σ, corresponding to the e_λ ranges in Figure 3. The different co-

Table 3. C.l.f. parameters values (cm^{-1}) of silylamido complexes of Ti, V, and Cr

		Titanium		Vanadium	Chromium
'Trend 1'					
	Σ	30 700		30 700	30 700
	e_σ(N)	6 400		7 100	8 500
	$e_{\pi\perp}$(N)	6 400		6 400	5 100
	e_σ(void)	−3 750		−4 900	−5 050
'Trend 2'					
	Σ	25 000*		32 000	29 000
	e_σ(N)	11 000	3 000	7 700	6 800
	$e_{\pi\perp}$(N)	1 500	7 500	6 400	5 750
	e_σ(void)	−6 250	−3 250	−5 150	−4 325
'Constant e_σ(N)'					
	Σ	30 000		32 000	30 000
	e_σ(N)	7 700		7 700	7 700
	$e_{\pi\perp}$(N)	5 150		6 400	5 500
	e_σ(void)	−4 275		−5 150	−4 800

* Two sets of parameters are associated with this trace value, see Figure 3(*a*).

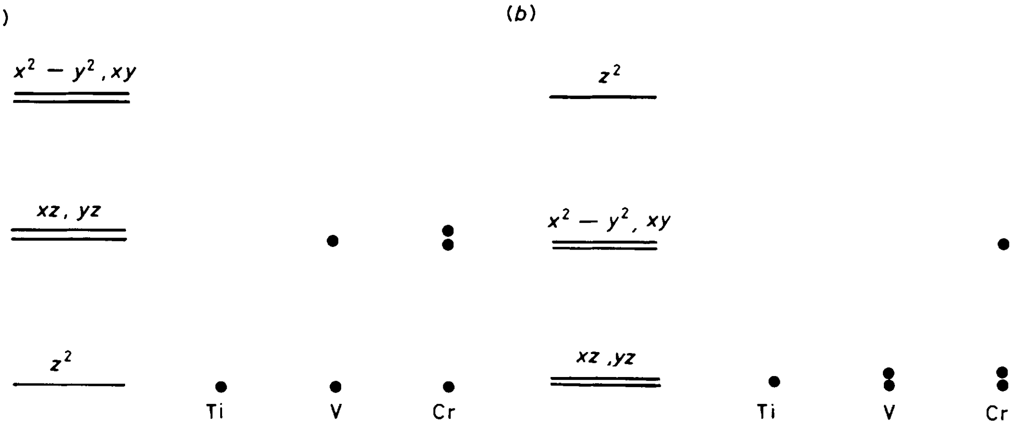

Figure 7. (*a*) Orbital occupancies in the three-co-ordinate complexes. Orbitals are labelled in D_{3h} speciation or predominant D_3 speciation. (*b*) Orbital occupancies in trigonal-bipyramidal symmetry

ordinations in the present two series will be shown to involve different ligand-field traces, so that our discussions of each are developed separately: they do, however, employ the same principles of electroneutrality and bonding.

As reviewed in the Introduction, values of the ligand-field trace for metal(II) systems vary somewhat between ligand types but are otherwise found to be essentially independent of co-ordination number, geometry, or metal. It is natural, therefore, to look for similar behaviour in the present metal(III) complexes. The broken lines in Figure 6 define two trends in Σ values which, we believe, exemplify the whole range of possible variations implied by the Σ ranges shown in the figure. In trend 1, we consider a constant trace across the series which, we note, is possible only for Σ *ca.* 31 500 cm^{-1}. Values of e_λ corresponding to that Σ value are listed in Table 3. Also given are e_λ values associated with trend 2 of Figure 6 achitypal of all other possible variations within the series. While the idea of a constant trace is attractive by comparison with those determined for metal(II) systems, we now seek support for trend 1 over trend 2 that does not depend upon that analogy. Two obvious features characterize any traverse of a series of complexes [ML_n] (M = $\mathrm{Ti^{III}}$, $\mathrm{V^{III}}$, or $\mathrm{Cr^{III}}$). One is that the effective nuclear charge in the metal increases as we increase the atomic number and the other concerns the varying *d* orbital occupancy. Increasing effective nuclear charge appears always to be associated with larger ligand-field parameters; as, for example, along the series $\mathrm{Co^{II}}$, $\mathrm{Ni^{II}}$, $\mathrm{Cu^{II}}$ or as metal(II) is replaced by metal(III). Accordingly, from the variation in the effective nuclear charge in the present series, we expect all e_λ values to increase. For those parameter values in Table 3 associated with trend 1, such is observed for e_σ(N) but not for $e_{\pi\perp}$(N). That arises, we propose, in reaction to the changing *d* orbital occupation along the series. From Figure 7(*a*), we observe how the successive replacement of $\mathrm{Ti^{III}}$ by $\mathrm{V^{III}}$ and $\mathrm{Cr^{III}}$ involves a steady increase in the occupation of those metal orbitals (*xz*, *yz*) associated with π interactions with the silylamido ligands. Employing the current view of the significance of ligand-field parameters, that increased orbital occupancy increasingly frustrates the metal–ligand bonding proper so that, despite the general increase in effective nuclear charge, M–L π bonding diminishes; in turn, this is reflected in decreasing $e_{\pi\perp}$(N) parameter values. Some strengthening of M–L σ bonding might well accompany this trend, in response to the demands of the electroneutrality principle operating on both metal and ligands but, if so, this cannot be disentangled from the trend in e_σ(N) values already discussed. The increasing magnitude of the (negative) e_σ(void) parameter along the series

Table 4. Comparisons between observed and calculated properties for the silylamido complexes $[M\{N(SiMe_3)_2\}_3]$

	Titanium		Vanadium		Chromium	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.[a]
Transition energies of maximum spin multiplicity/cm^{-1}	17 400	17 708		36 449		36 269
		17 510	24 700	21 868		26 172
				21 736		24 636
	4 800	4 635	19 200	19 248	14 800	14 772
			15 900	16 161		14 574
			ca. 11 000	10 418	11 800	12 853
				10 262		11 399
						11 327
				3 040	*ca.* 8 400	8 374
				37		
Principal g-values $g_{\parallel}$	1.933	2.00			*ca.* 2	*ca.* 2[b]
Principal g-values $g_{\perp}$	1.869	1.87			*ca.* 4	*ca.* 4
Zero-field splitting, D/cm^{-1}					−1.85	−1.842
e_{σ}(N)/cm^{-1}		6 400		7 100		8 500
$e_{\pi\perp}$(N)/cm^{-1}		6 400		6 400		5 100
e_{σ}(void)/cm^{-1}		−3 750		−4 900		−5 050
Σ/cm^{-1}		30 700		30 700		30 700
B/cm^{-1}		—		680		830
C/cm^{-1}		—		—		3 000
ζ/cm^{-1}		130		200		175
k		0.85		—		—
Orbital energies/cm^{-1} (ζ = 0)		17 604		20 066		19 178
		17 602		20 063		19 170
		4 599		6 476		5 490
		4 594		6 471		5 486
		0		0		0

[a] Results calculated with full d^3 basis: only spin-quartet transition energies are reported. [b] For $\zeta = 0$, $g_{\parallel} = 2.0$, and $g_{\perp} = 4.0$ exactly.

is rationalized in two ways. Increasing effective nuclear charge increases the penetration of the metal 4*s* orbital and decreases the 3*d*–4*s* promotion energy, leading to an increase in the e_{σ}(void) value.[2–4] Secondly, increasing polarization of the ligand σ functions along the series increases not only the overall ligand-field potential but also its departure from spherical symmetry. That part of the overall, non-spherical potential within a co-ordinationally void cell will be negative and of a magnitude which should increase as the positive potential increases in adjacent non-void cells. Empirically these ideas are supported not only by the trends in Table 3 that we seek to rationalize but also by the generally greater e_{σ}(void) values observed in metal(III) complexes relative to metal(II).

Overall, therefore, the variations in the individual e_{λ} parameter associated with the constant trace of *ca.* 31 500 cm^{-1} are wholly compatible with general principles employed to interpret ligand-field parameters *and* bonding throughout a wide variety of transition-metal complexes. On the other hand, we are quite unable to account for the variations in e_{λ} parameters associated with trend 2 as shown in Table 3. A third set included in the table is based upon the notion of a constant (transferable) value for e_{σ}(N). While this does yield a near-constant value for the ligand-field trace, we consider it unsatisfactory in terms of expected variations with respect to effective nuclear charge. In summary: on the balance of probabilities, we propose that the ligand-field parameters of trend 1 in Table 3 best represent this series of three-co-ordinate complexes. Correlated variations in these parameter values of some 10% would fit experiment equally well without any significant change in either the ligand-field trace or in the semi-quantitative description of bonding trends offered for these species. Details of the reproduction of all

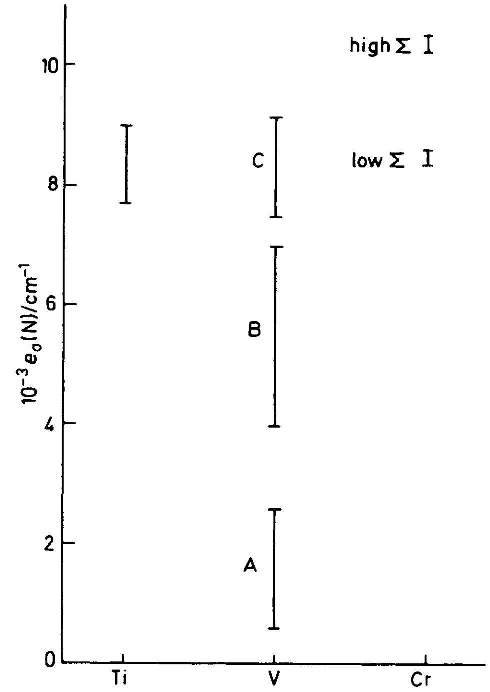

Figure 8. Bounds of possible e_{σ}(N) values in $[MCl_3(NMe_3)_2]$ complexes. Bounds for the vanadium complex refer to c.l.f. refinements for assignments A, B, and C (see text); and for the chromium complex, to refinements yielding 'high' and 'low' ligand-field traces

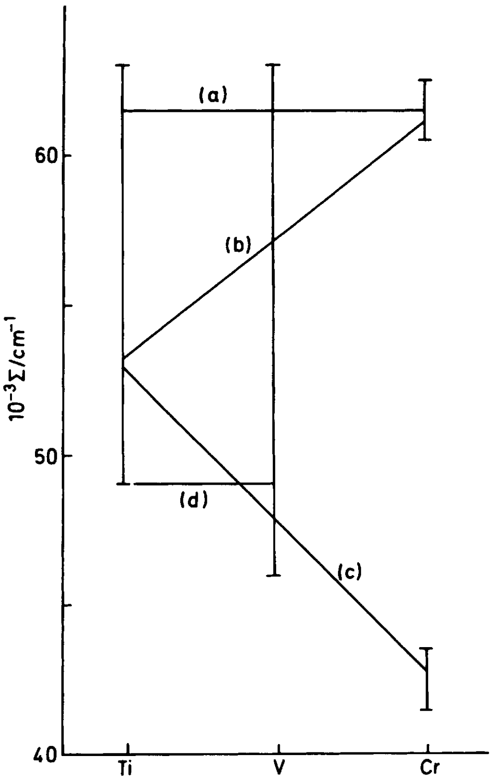

Figure 9. $[MCl_3(NMe_3)_2]$: bounds of possible ligand-field trace values, after discarding assignments A and B for the vanadium complex. Thin lines label trends discussed in the text

Table 5. Optimal c.l.f. parameter values for $[MCl_3(NMe_3)_2]$ giving selected ligand-field traces (cm^{-1})

		Titanium	Vanadium	Chromium
Trend (a)				
	Σ	61 000	61 000	61 000
	e_σ(N)	8 900	8 900	10 400
	e_σ(Cl)	5 300	5 300	4 500
	e_π(Cl)	4 600	4 600	4 500
Trend (b)				
	Σ	50 000	56 000	61 000
	e_σ(N)	7 822	8 406	10 350
	e_σ(Cl)	5 300	5 300	4 500
	e_π(Cl)	3 076	3 881	4 467
Trend (c)				
	Σ	58 000	50 000	42 000
	e_σ(N)	8 572	7 802	8 450
	e_σ(Cl)	5 300	5 300	4 500
	e_π(Cl)	4 159	3 083	1 933
Trend (d)				
	Σ	50 000	50 000	
	e_σ(N)	7 822	7 802	
	e_σ(Cl)	5 300	5 300	
	e_π(Cl)	3 076	3 083	

experimental data with these parameter values are listed in Table 4.

Turning now to the five-co-ordinate species, we present in Figure 8 ranges of e_σ(N) values established for the three chloro complexes. One range has been established for $[TiCl_3(NMe_3)_2]$, one for each of the three assignments A, B, C in $[VCl_3(NMe_3)_2]$, and two reasonably well-determined alternatives for $[CrCl_3(NMe_3)_2]$. Let us consider what *trends* might be expected for this parameter by reference to the same general bonding principles employed above. First, other things being equal, all e_λ parameters are expected to increase as we traverse the transition-metal series from left to right in response to increasing effective nuclear charge. Overlying this once more will be the effects of the changing occupation of the *d* orbitals. Referring to the electron occupancies sketched in Figure 7(*b*) we note that the d_{z^2} orbital remains vacant throughout this short series so that no hindrance to σ bond formation between metal *s* and ligand functions is involved. However, a slight increase in repulsion is expected within the M–Cl π framework to accompany the change from d^1 to d^2 and a larger repulsion as the third electron of chromium occupies the equatorial σ bonding orbitals. In response to the demands of the Electroneutrality Principle, we expect an increase in axial σ bonding, over and above that due to changes in the effective nuclear charge, in compensation for these increases in equatorial steric hindrance. These same arguments have been invoked[8,28] to rationalize changing differences between axial and equatorial bonding and ligand fields in trigonal-bipyramidal complexes of various metal(II) complexes. Altogether, therefore, we expect e_σ(N) values along the present series to increase from titanium(III) to vanadium(III) and probably even more from vanadium(III) to chromium(III). These expectations strongly disfavour assignments A and B for the vanadium complex which, by reference to Figure 8, are characterized by low e_σ(N) values. They also suggest that the 'high trace' fit for the chromium complex is to be preferred. Furthermore, as assignment C is determined by the three best-resolved features in the reported spectrum, any residual uncertainty attaching to the complex region between 11 000 and 16 000 cm^{-1} loses importance.

In Figure 9 are plotted the ranges of the ligand-field trace values, having discarded those for assignments A and B for the vanadium system. We now *propose*, in view of our experience with the constancy of Σ values with respect to metal(II) systems, that these traces should either vary little along the series or, if not, should vary smoothly and roughly linearly. We now examine the detailed c.l.f. parameter values corresponding to four trends indicated in Figure 9. Trend (a) describes a constant trace throughout the series consistent with the 'high trace' solution for the chromium complex; trend (b) considers an essentially linear increase from titanium to chromium, again consistent with the 'high trace' choice; trend (c) selects the 'low trace' choice for chromium which can only be accommodated within a linear trend that decreases from titanium; and trend (d) considers the case in which we discount the analysis of the chromium system and presume a constant trace from titanium to vanadium of the lowest value possible so as to approach the value of 46 000 cm^{-1} obtained for the tris(ethylenediamine)-chromium(III) chromophore. The present analysis for $[CrCl_3(NMe_3)_2]$ is possibly less exact in its reproduction of the spectrum, the spectral contour of which was not reported, and might be considered a little too uncertain upon which to rest our ultimate selection of a high trace. The c.l.f. parameter sets corresponding to these four trends are collected together in Table 5.

Consider first the parameter values for trend (a). The variation in e_σ(N) along the series is comprehensible in terms of the increasing effective nuclear charge and changing orbital occupancies discussed above. So too is the variation in e_σ(Cl), the same for all trends (a)—(d), of course, in that *d* electron occupancy of the equatorial σ orbitals only begins at chromium, so weakening the in-plane metal–ligand interaction in that step. At the same time, rather less pronounced effects upon bond

Table 6. Comparisons between observed and calculated properties for the trigonal-bipyramidal series

	Titanium		Vanadium		Chromium	
(*a*) $[MCl_3(NMe_3)_2]$	Obs.	Calc.	Obs.	Calc.^{a}	Obs.	Calc.^{b}
Transition energies of maximum spin multiplicity/cm^{-1}	15 100	15 078		22 224	30 200	30 053
		6 310	20 100	21 837		27 057
	6 100	6 001		20 108		26 282
		376		19 764	23 200	23 169 (2)^c
				19 521		18 996
			ca. 16 500	17 386 (1)^c	17 600	17 805
			13 000	12 978 (1)^c		17 483
				12 930 (1)^c	13 000	12 954 (2)^c
				12 918 (1)^c	10 100	10 283
			7 100	7 032		9 903
				6 892		559
			4 900	4 933		
				4 627		
10^{-4} Mean susceptibility/c.g.s.u.^{d} (temp./K)	12 (298)	12 (298)	30 (298)	33 (298)	63 (298)	58 (298)
	16 (213)	16 (213)			80 (233)	73 (233)
	21 (152)	21 (152)			121 (153)	108 (153)
	33 (85)	34 (85)			191 (93)	173 (93)
$e_\sigma(N)/cm^{-1}$		8 900		8 900		10 400
$e_\sigma(Cl)/cm^{-1}$		5 300		5 300		4 500
$e_\pi(Cl)/cm^{-1}$		4 600		4 600		4 500
Σ/cm^{-1}		61 000		61 000		61 000
B/cm^{-1}		—		700		910
C/cm^{-1}		—		2 100		3 100
ζ/cm^{-1}		150		150		150
k		0.75		0.75		0.5
Orbital energies/cm^{-1} ($\zeta = 0$)		15 057		15 009		18 048
		6 180		6 132		5 911
		6 091		6 062		5 408
		345		275		1 222
		0		0		0
(*b*) $[MBr_3(NMe_3)_2]$						
Transition energies of maximum spin multiplicity/cm^{-1}	14 100	14 243		21 411		
		5 299	18 700	21 063		
	5 100	4 970		18 717		
		354		18 479		
				17 897		
			ca. 14 500	13 950 (1)^c		
			13 500	13 585 (1)^c		
				13 544 (1)^c		
			10 800	10 420 (1)^c		
				10 409 (1)^c		
			6 100	6 265		
				6 137		
			4 200	4 156		
				3 851		
10^{-4} susceptibility/c.g.s.u.^{d} (temp./K)	12 (298)	12 (298)	29 (298)	33 (298)		
	16 (204)	17 (204)				
	24 (125)	24 (125)				
	30 (93)	31 (93)				
$e_\sigma(N)/cm^{-1}$		8 600		8 750		
$e_\sigma(Br)/cm^{-1}$		4 400		4 500		
$e_\pi(Br)/cm^{-1}$		4 300		4 200		
Σ/cm^{-1}		56 200		56 200		
B/cm^{-1}		—		660		
C/cm^{-1}		—		2 900		
ζ/cm^{-1}		150		150		
k		0.75		0.75		
Orbital energies/cm^{-1} ($\zeta = 0$)		14 221		14 696		
		5 184		5 232		
		5 040		5 139		
		322		251		
		0		0		

[a] Calculations in full d^2 basis but only those spin-singlets fitting observed transitions are reported. [b] Calculations in full d^3 basis but only those spin-doublets fitting observed transitions are reported. [c] Spin multiplicities given in parentheses. [d] C.g.s.u. = $4\pi \times 10^{-6}$ m^3 mol^{-1}.

strength, and hence upon ligand-field parameters, are to be expected with respect to the metal–chlorine π bonding; however, any change expected from the variation in orbital occupancy is expected to increase from d^1 to d^2 but not markedly from d^2 to d^3. These variations taken together with the underlying change in the effective nuclear change will tend to cancel. Overall, the c.l.f. parameter variations associated with a constant high trace [trend (a)] appear to be wholly compatible with general bonding principles. The same is probably true of the parameters associated with trend (b), although the increases in e_σ(N) and e_π(Cl) might be considered to be greater than expected. Subjectively, we would prefer those for trend (a) over trend (b), if only because of the constancy in Σ values established for metal(II) systems. With much greater confidence we would reject the parameter sets for trend (c) by reference to both e_σ(N) and e_π(Cl). We therefore reject the 'low trace' fit for the chromium complex also.

Altogether, by comparison with the essentially constant trace established for silylamido complexes and with the well established constant trace of metal(II) complexes at the other end of the transition series, we favour the constant trace for the five-co-ordinate species of *ca.* 61 000 cm^{-1}, if the analysis for [$CrCl_3(NMe_3)_2$] is reliable, or at some value between 50 000 and 61 000 cm^{-1}, if not [see Table 5, trend (d)].

Arguments for the bromo analogues of titanium and vanadium would follow similar lines. The characteristic differences between the chloro and bromo complexes are that $e_\sigma(\mathrm{Br}) < e_\sigma(\mathrm{Cl})$; $e_\pi(\mathrm{Br}) < e_\pi(\mathrm{Cl})$; $e_\sigma(\mathrm{N})_{\mathrm{Br}} < e_\sigma(\mathrm{N})_{\mathrm{Cl}}$; and $\Sigma(\mathrm{Br}) < \Sigma(\mathrm{Cl})$. That σ and π c.l.f. parameters are less for bromo complexes than for chloro occasions no surprise: the relative trace values seem to accord with similar (unpublished) findings for metal(II) complexes. We presume that lower e_σ(N) values for the bromo complexes reflect a greater steric hindrance for these axial groups by the more bulky equatorial ligands.

Finally, the quality of the reproduction of experimental data throughout this series is presented in Table 6 for suitably selected optimal parameter sets. The parameter selections made here are not intended to prejudice the conclusions and uncertainties expressed earlier. Included in Tables 4 and 6 are corresponding orbital energies.

Acknowledgements

We are most grateful to Professor D. C. Bradley for the loan of 'raw' experimental electronic spectral traces for the silylamido complexes. N. D. F. thanks the S.E.R.C. for financial support.

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Received 29th October 1987; *Paper* 7/1927