Ligand Field Theory for Pentacoordinate Molecules. II. A Crystal Field— Spin–Orbit Coupling Treatment of the d^1, d^3, d^6, and d^8 Configurations in Trigonal-Bipyramidal Molecules and the Magnetic Properties of E Ground Terms

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The energy levels for a d^1 ion under the combined action of spin–orbit coupling and a crystal field of trigonal-bipyramidal symmetry have been deduced and the form of the temperature variation of the magnetic moment for the $^2E''$ ground state, using both the zero-order and first-order corrected wave functions, is given. In addition, the magnetic properties anticipated for the $^4E'$ (d^3), $^5E''$ (d^6), and $^3E'$ (d^8) ground states have been evaluated. It is shown that the magnetic properties of the two compounds $TiBr_3 \cdot 2N(CH_3)_3$ and $TiCl_3 \cdot 2N(CH_3)_3$ cannot be explained on the basis of a D_{3h} ligand field and that a small additional low-symmetry ligand field component (in the xy plane) must be present. The magnetic properties anticipated for C_{2v} symmetry have also been evaluated and it appears that the splitting of the $^2E''$ state in these molecules is of the order of 300 cm^{-1}. A similar situation also occurs in $CrCl_3 \cdot 2N(CH_3)_3$ although, here, the deviation from that predicted for the $^4E'$ state is much larger and a low-symmetry component of at least 2000 cm^{-1} must be invoked to explain the observed temperature-independent, spin-only moment. The magnetic properties of some recently reported species of C_{3v} symmetry are discussed in the light of the predicted behavior for the d^6 and d^8 configurations.

Introduction

While many of the pentacoordinate complexes of the transition elements that have been isolated in recent years have generally been characterized (in the absence of an X-ray structure analysis) by the study of their electronic spectra, whose assignments have been facilitated by the crystal field energy level diagrams and calculations now available,[2-4] no comparable study has been made of their magnetic properties. Moreover, apart from the pentachlorocuprate ion[5] and very recently some other trigonal-bipyramidal complexes of copper,[6] no theoretical evaluation of the anticipated magnetic moments for other configurations and their temperature dependence has been given. One of the treatments for the Cu^{2+} ion in D_{3h} symmetry (trigonal-bipyramidal geometry) would appear to be in error, as the ordering of the one-electron orbitals yields a doublet, rather than a singlet, as ground state.[7]

Of those molecules that can be classed as possessing trigonal-bipyramidal geometry, only two groups have sufficient symmetry to make any sort of detailed treatment of their magnetic properties feasible, and these, which are of the "high-spin" variety, are the trimethylamine adducts of various trihalides of titanium, va-

nadium, and chromium,[8,9] and molecules containing the tetradentate ligands, tris(2-aminoethyl)amine and tris(2-dimethylaminoethyl)amine, which confer pentacoordination on the metal ion.[10,11] The polyhedra in these molecules have, or are capable of possessing, D_{3h} or C_{3v} symmetry,[12] respectively, and hence the ground states for certain configurations can retain some orbital degeneracy, *i.e.*, they are of E symmetry. In order to evaluate the magnetic properties, it is necessary to consider the manner in which this remaining orbital degeneracy is affected on inclusion of spin–orbit coupling and this is treated for the d^1 configuration in detail and for the ground states, for the other d^n configurations of relevance.

The trimethylamine adducts of the metal trihalides have been shown by X-ray analysis to be trigonal bipyramidal, with, in the case of the titanium and chromium compounds, deviations from the idealized D_{3h} geometry.[13,14] Detailed assignments of the electronic spectra of the titanium and vanadium compounds have been made on the basis of the idealized symmetry,[4] but in the case of the chromium compound it was not possible to obtain a reasonable fit for this model. Analysis of the magnetic data has indicated the presence of a large additional low-symmetry, ligand field component.

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A further paper in this series will deal with the magnetic properties of those pentacoordinate molecules with nondegenerate ground states, *i.e.*, terms of A symmetry, and it will be shown that the magnetic properties of $VX_3 \cdot 2N(CH_3)_3$ species are consistent with D_{3h} geometry.

Experimental Section

Preparations.—Trichlorobis(trimethylamine)titanium(III) and trichlorobis(trimethylamine)chromium(III) were prepared as previously described.[8,9]

Magnetic Susceptibility Measurements.—Measurements were made over a temperature range on a Newport Instruments variable-temperature balance system, based on the instrument originally designed by Figgis and Nyholm.[15] Solid $HgCo(CNS)_4$ was used as the calibrant. The Gouy tube was constructed from a Q and Q B5 socket so that air- and moisture-sensitive compounds could be loaded in an atmosphere of dry nitrogen on the vacuum line. The measurements were performed with the Gouy tube suspended in an atmosphere of dry nitrogen and were made at two different field strengths. The usual diamagnetic corrections were applied[16] and the results are given in Table I, χ_m' being the corrected molar susceptibility.

TABLE I

MAGNETIC DATA FOR $MCl_3 \cdot 2N(CH_3)_3$ COMPLEXES

—TiCl₃·2N(CH₃)₃, θ = 41°—			—CrCl₃·2N(CH₃)₃, θ = 7°—		
Temp, °K	$10^6\chi_m'$, cgsu	μ_{eff}, BM	Temp, °K	$10^6\chi_m'$, cgsu	μ_{eff}, BM
298.2	1195	1.69	298.2	6,305	3.88
288.2	1223	1.68	291.9	6,448	3.88
273.2	1279	1.67	283.2	6,646	3.88
253.2	1366	1.66	273.2	6,899	3.89
233.1	1459	1.65	253.2	7,424	3.88
213.1	1574	1.64	233.2	8,049	3.88
193.2	1709	1.63	213.2	8,794	3.88
173.2	1859	1.60	193.2	9,661	3.87
153.2	2055	1.59	173.2	10,753	3.86
133.0	2299	1.56	153.1	12,123	3.86
113.0	2606	1.53	133.0	13,873	3.84
84.9	3280	1.49	113.0	16,153	3.82
			93.0	19,110	3.77

The results for tribromobis(trimethylamine)titanium(III), which are very similar to those for the chloro compound, have been given previously.[17] The magnetic properties of the nickel complex $Ni(Me_6tren)Cl^+$ have been studied at three temperatures—79 and 192°K and room temperature[11]—while for the corresponding iron complex only a room-temperature magnetic moment has been reported.[10]

Theory and Calculations

The splitting pattern of the free-ion d orbitals in the crystal or ligand field arising in a pentacoordinate transition metal complex of D_{3h} or C_{3v} symmetry is by now well known and the energies of the two doubly degenerate levels e′ ($d_{x^2-y^2}$ and d_{xy}) and e″ (d_{xz} and d_{yz}) (both of e symmetry in C_{3v}) and the single level a_1' (d_{z^2}) have been given in terms of the crystal field parameters Ds and Dt.[4] Similarly the splittings of the free-ion terms arising for the various d-electron configurations have been evaluated.

(15) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 331 (1959).
(16) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960.
(17) D. J. Machin, K. S. Murray, and R. A. Walton, *J. Chem. Soc., A*, 195 (1968).

In these calculations, solely the crystal field states arising from the D and F free-ion terms, in the weak-field model, will concern us. The ground state is orbitally doubly degenerate, *i.e.*, E′ or E″, for the configurations d^1, d^3, d^6, and d^8 in the weak-field model, and these correspond to the configurations of unevenly filled subshells in the infinitely strong crystalline field, *viz.*, (e″), (e″)²(e′), (e″)³(e′)²(a_1'), and (e″)⁴(e′)³-(a_1'). For low-spin complexes, orbitally degenerate ground states of type ²E″ or ²E′ arise for the configurations d^3 [(e″)³], d^5 [(e″)⁴(e′)], and d^7 [(e″)⁴(e′)³]. Low-spin pentacoordinate complexes of cobalt(II) and iron(III) of presumably C_{3v} (or approximately C_{3v}) symmetry with multidentate ligands have been isolated and studied, and assignments of the bands in their electronic spectra made.[3] One of these complexes containing "low-spin" cobalt(II), $CoP(C_6H_5-P(C_6H_5)_2)_3Cl^+$, has been structurally characterized, but the deviation of the polyhedron from C_{3v} symmetry is large.[18]

The perturbation of a free-ion spectroscopic term by the combined effects of a crystal field, spin–orbit coupling and an external magnetic field can be represented by the Hamiltonian

$$\mathcal{H} = V_{CF} + \lambda \mathbf{L} \cdot \mathbf{S} + \beta \mathbf{H} \cdot (k\mathbf{L} + 2\mathbf{S}) \qquad (1)$$

where V_{CF} is the crystal field potential, λ is the spin–orbit coupling constant for the metal ion, and the spin–orbit term is given by

$$\lambda \mathbf{L} \cdot \mathbf{S} = \lambda(L_z S_z + {}^1/_2(L_+ S_- + L_- S_+)) \qquad (2)$$

The parameter k in the Zeeman operator is the "orbital reduction factor" and has been related to the degree of mixing of metal and ligand orbitals. Covalency effects are also taken into account by utilization of a value for λ lower than the relevant free-ion value λ_0. While there is no *a priori* reason why k and the ratio λ/λ_0 should be equal, one would expect the two quantities to be correlated. Accordingly in these calculations we have taken them to have the same value, wherever they are introduced, and moreover we have assumed k to be isotropic.

For first-row transition elements, to obtain the eigenvalues for the spin–orbit perturbation, we can use the strong crystalline field eigenfunctions as bases, since the first term in (1) is greater in magnitude than the second term.

To evaluate the magnetic properties for anisotropic systems we use the Zeeman operators $\mu_{||} = \beta(kL_z + 2S_z)$ and $\mu_\perp = \beta(kL_x + 2S_x)$. The principal susceptibilities $\chi_{||}$ and $\chi_\perp$ were calculated from the first- and second-order Zeeman energies and the usual Van Vleck equation,[19] and the average effective magnetic moment (since we are concerned with powder samples) was obtained from the relations $\bar{\chi} = {}^1/_3(\chi_{||} + 2\chi_\perp)$ and $\chi = (N\beta^2/3kT)\mu_{eff}^2$.

(18) T. L. Blundell, H. M. Powell, and L. M. Venanzi, *Chem. Commun.*, 763 (1967).
(19) J. H. Van Vleck, "Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932.
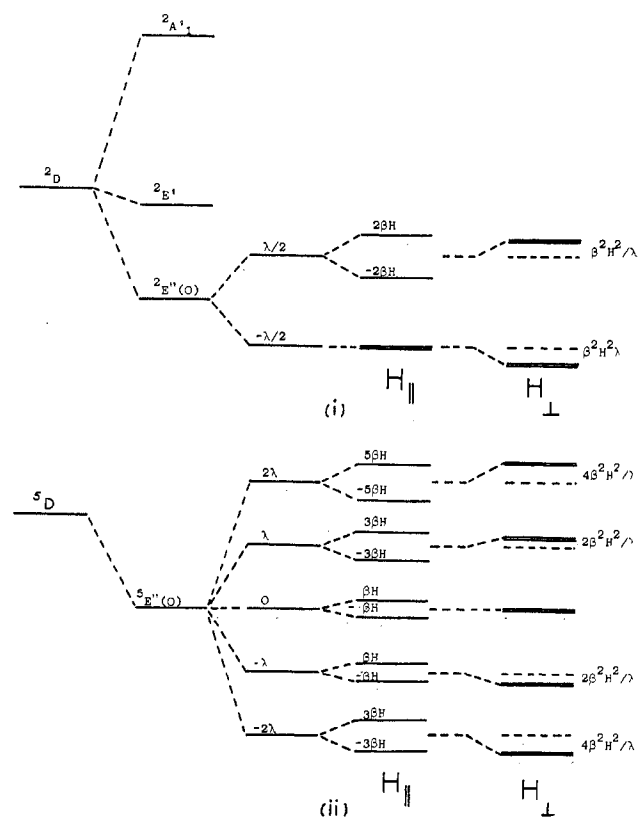
Figure 1.—Free-ion D terms under the successive influences of a weak ligand field of trigonal-bipyramidal D_{3h} symmetry, spin–orbit coupling, and a magnetic field: (i) $^2E''$ term; (ii) $^5E''$ term.

(1) The d^1 Configuration.—For this configuration the appropriate basis eigenfunctions and their representations in the double group, D_3,[20] are

$^2E''$	$\|\pm1,\ \mp^1/_2\rangle$	$\Gamma_4{}^n$
	$\|\pm1,\ \pm^1/_2\rangle$	$(\Gamma_5+\Gamma_6)^n$
$^2E'$	$\|\pm2,\ \mp^1/_2\rangle$	$(\Gamma_5+\Gamma_6)^n$
	$\|\pm2,\ \pm^1/_2\rangle$	$\Gamma_4{}^n$
$^2A_1'$	$\|0,\ \pm^1/_2\rangle$	$\Gamma_4{}^n$

where $n = a$ or b. Operating with (2) we get eq 3 for

$\Gamma_4{}^n$ ($^2E''$) $\Gamma_4{}^n$ ($^2A_1'$)

$$\begin{vmatrix} -(\lambda/2) + Ds - 4Dt - E & (3/2)^{1/2}\lambda \\ (3/2)^{1/2}\lambda & 2Ds + 6Dt - E \end{vmatrix} = 0$$

$(\Gamma_5+\Gamma_6)^n$ ($^2E''$) $(\Gamma_5+\Gamma_6)^n$ ($^2E'$)

$$\begin{vmatrix} (\lambda/2) + Ds - 4Dt - E & \lambda \\ \lambda & -\lambda - 2Ds + Dt - E \end{vmatrix} = 0 \tag{3}$$

$\Gamma_4{}^n$ ($^2E'$) $|\lambda - 2Ds + Dt - E| = 0$

the blocked form of the secular determinant, which is diagonal in the crystal field parameters Ds and Dt. In

(20) The characters for the "two-valued" representations of the double group D_3 are, using Bethe's notation, Γ_4, Γ_5, and Γ_6, and are listed by J. S. Griffith, "Theory of Transition Metal Ions," Cambridge University Press, London, 1961, Appendix 2, p 384.

TABLE II

THE GROUND-STATE EIGENFUNCTIONS FOR $^2E''$, $^5E''$, $^4E'$, AND $^3E'$, THEIR REPRESENTATIONS IN D_3, AND THE MATRIX ELEMENTS OF THE ZEEMAN OPERATORS, WITH $k = 1$

	M_S	Representation	$\mu_{\|\|}$	$\mu_\perp$	M_S	Representation	$\mu_{\|\|}$	$\mu_\perp$	
d^1	$\pm^1/_2$	$\Gamma_5+\Gamma_6$	±1	1	$\pm^3/_2$	Γ_4	±5	2	
	$\mp^1/_2$	Γ_4	0		$\pm^1/_2$	Γ_4	±3	$3^{1/2}$	d^3
					$\mp^1/_2$	$\Gamma_5+\Gamma_6$	±1	2	
	±2	$\Gamma_1+\Gamma_2$	±5	2	$\mp^3/_2$	Γ_4	∓1		
d^6	±1	Γ_3	±3	$6^{1/2}$					
	0	Γ_3	±1	$6^{1/2}$	±1	Γ_3	±4	$2^{1/2}$	
	±1	$\Gamma_1+\Gamma_2$	∓1	2	0	Γ_3	±2	$2^{1/2}$	d^8
	∓2	Γ_3	∓3		∓1	$\Gamma_1+\Gamma_2$	0	$2^{1/2}$	

the first-order approximation, then, the $^2E''$ ground state of the d^1 configuration is split into two Kramers doublets separated by an energy λ. Calculations of magnetic moment, μ_{eff}, for this configuration were performed using both zero-order eigenfunctions and the first-order corrected eigenfunctions derived from (3). The matrix elements for the basis set of orbitals restricted to the $^2E''$ ground state are for the "parallel" operator, $\mu_{\|\|}$, $\pm(1 + k)\beta$ and $\pm(1 - k)\beta$ for the $(\Gamma_5 + \Gamma_6)$ and Γ_4 eigenfunctions, respectively, while the non-zero matrix element for $\mu_\perp$ is that between corresponding members of each set.

With $k = 1$, the ground state is a "nonmagnetic" doublet, as for the octahedral $^2T_{2g}$ term of d^1; while using eigenfunctions correct to first order in λ, there is a small splitting of the ground level and a residual magnetic moment, which is also the situation when $k < 1$. The matrix elements for $k = 1$ are listed in Table II and the relevant energy level diagram is illustrated in Figure 1(i). The principal susceptibilities, setting $\lambda/kT = x$, are set out in Table III.

(2) The Configurations d^6, d^3, and d^8.—The free-ion ground states ^5D, ^4F, and ^3F for these three configurations are split by a D_{3h} ligand field to give, respectively, $^5E''$, $^4E'$, and $^3E'$ weak crystal field ground states. (In C_{3v} symmetry these all transform as E.) Inclusion of spin–orbit coupling removes the degeneracy of each of these terms giving sets of doubly degenerate levels in each instance. The first-order energies on inclusion of spin–orbit coupling (referred to the parent crystal field ground state as zero) are illustrated in Figures 1(ii) and 2.

The relevant eigenfunctions, denoted by their M_S values and having $M_L = \pm1$ for the E'' states and ±2 for the E' states, together with their representation in the D_3 double group are listed in Table II. Also included are the matrix elements of the two Zeeman effect operators calculated for $k = 1$. The only non-zero elements for $\mu_\perp$ are those between "neighboring" eigenfunctions, as for d^1, so only second-order Zeeman energies are involved in $\chi_\perp$.

The splitting patterns for the three states and the relevant Zeeman energies are illustrated in Figures 1 and 2, and the expressions for $\chi_{\|\|}$ and $\chi_\perp$ derived from these energies are listed in Table III.

Table III

Principal Susceptibilities for the $^2E''$, $^5E''$, $^4E'$, and $^3E'$ Ground Terms $(x = \lambda/kT)^a$

	$\chi_{\parallel}$	$\chi_{\perp}$
$^2E''$	$12/(1 + e^x)$	$[6 \tanh (x/2)]/x$
$^5E''$	$\dfrac{3(25e^{-2x} + 9e^{-x} + 1 + e^x + 9e^{2x})}{e^{-2x} + e^{-x} + 1 + e^x + e^{2x}}$	$\dfrac{(12/x)[2(e^{2x} - e^{-2x}) + (e^x - e^{-x})]}{e^{-2x} + e^{-x} + 1 + e^x + e^{2x}}$
$^4E'$	$\dfrac{3(25e^{-3x} + 9e^{-x} + e^x + e^{3x})}{e^{3x} + e^x + e^{-x} + e^{-3x}}$	$\dfrac{(3/x)[3(e^{3x} - e^{-3x}) + (e^x - e^{-x})]}{e^{3x} + e^x + e^{-x} + e^{-3x}}$
$^3E'$	$\dfrac{12(4e^{2x} + 1)}{e^{2x} + 1 + e^{-2x}}$	$\dfrac{6/x(e^{2x} - e^{-2x})}{e^{2x} + 1 + e^{-2x}}$

^{a} Neglecting the factor $(N\beta^2/3kT)$.
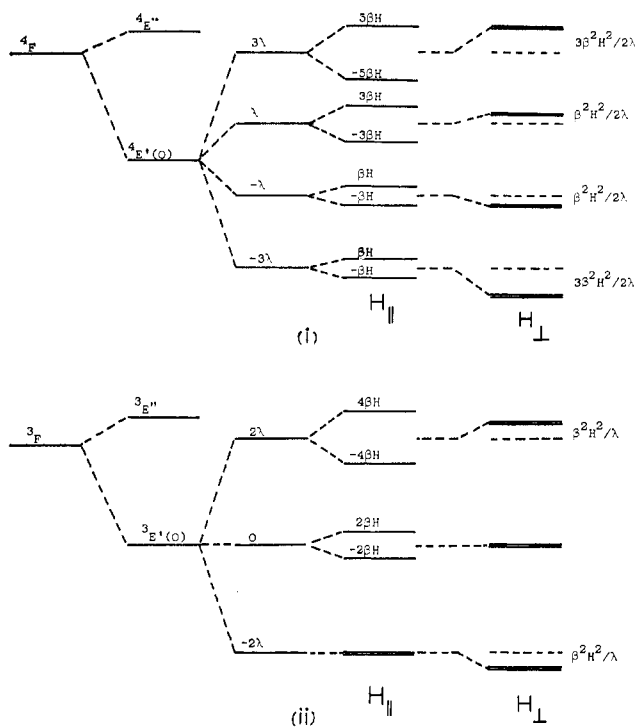
Figure 2.—Free-ion F terms under the successive influences of a weak ligand field of D_{3h} symmetry, spin–orbit coupling, and a magnetic field: (i) $^4E'$ term; (ii) $^3E'$ term.

Results and Discussion

The theoretical variations of the average effective magnetic moments with temperature, in the form of the parameter kT/λ, for the $^2E''$, $^5E''$, $^4E'$, and $^3E'$ states, as derived from the expressions in Table III, are illustrated in Figure 3 and the anticipated room-temperature values of μ_{eff} are indicated, for the free-ion values of λ. Since for the $^5E''$ and $^3E'$ state, the d configurations are more than half filled, λ is negative, and the energy level patterns in Figures 1(ii) and 2(ii) should thus be inverted. It is pertinent to note that in D_{3h} symmetry, the E' crystal field states arising from the ^4F and ^3F free-ion terms are the only states of this symmetry and consequently the magnetic properties in the medium-field situation, *i.e.*, before a term of
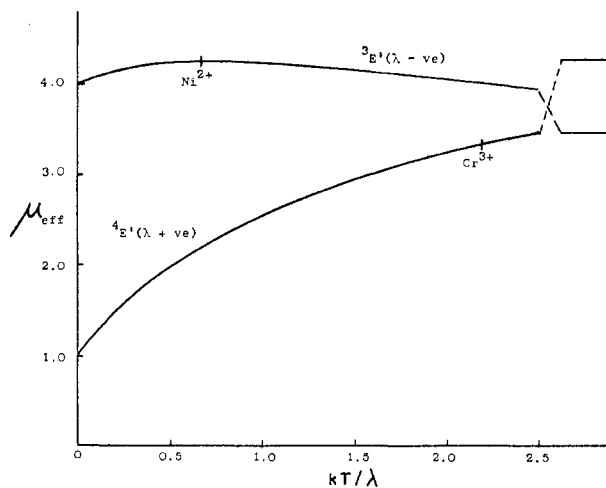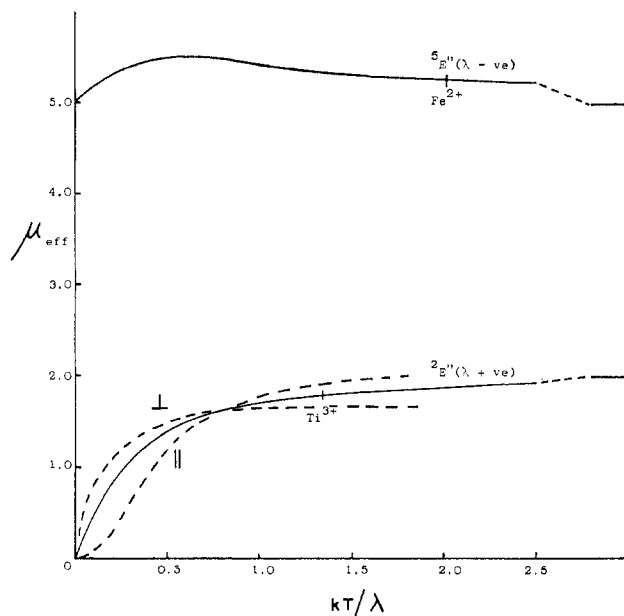

Figure 3.—The variation of μ_{eff} with kT/λ for (top) $^2E''$ and $^5E''$ terms and (bottom) $^4E'$ and $^3E'$ terms. The room-temperature values of μ_{eff} for Ti^{3+}, Fe^{2+}, Cr^{3+}, and Ni^{2+} are indicated. The principal moments for the $^2E''$ term are also indicated.

lower spin multiplicity becomes the ground level, are identical with the properties in the weak-field case. This is in contrast to the octahedral and tetrahedral instances where a T_1 state is the ground level.[21] Also included in Figure 1(i) is the variation of the principal moments for d^1, which gives an indication of the degree of anisotropy present in these systems.

(1) Magnetic Properties of d^1 and d^3 in D_{3h} Symmetry.—Considering first the d^1 configuration, it is seen that the temperature variation of the average magnetic moment predicted for the $^2E''$ state is very similar to that for the $^2T_{2g}$ octahedral term. It is therefore not surprising that a good "fit" was obtained for the magnetic properties of $TiBr_3 \cdot 2N(CH_3)_3$[17] with the theory for a distorted octahedral model.[22] On comparing the experimental temperature variation of moment for the two titanium complexes with that calculated, it can be seen that, as for octahedral titanium complexes, this is considerably less than that predicted. For the free-ion spin–orbit coupling constant of 155 cm^{-1}, it should not be possible to describe the susceptibility over such a large temperature range by means of the Curie–Weiss law. In fact, the Weiss constant is much smaller than anticipated and the law holds quite well, with $\theta \approx 40°$, for both bromide and chloride complexes.

While it seems evident that the experimental data at lower temperatures indicate the presence of a lower symmetry ligand field than D_{3h}, i.e., one in which the orbital degeneracy of the $^2E''$ ground state is lifted, it will be seen that this alone cannot account for the observed behavior completely. In order to "describe" the results at higher temperatures, it is necessary to consider both the use of an expanded-basis orbital set and to make an allowance for covalency effects by using a value for k less than unity. Consideration of electron delocalization, i.e., $k < 1$, has been considered in some detail for the t_{2g}^1 configuration and its inclusion leads to a smaller temperature variation of μ_{eff}.[22]

The results of calculations using the first-order corrected eigenfunctions derived from (3) with $k = 1.0$ are illustrated in Figure 4, the calculation being carried out for values of the crystal field parameters Ds and Dt of 420 and 1470 cm^{-1}, respectively.[23] Comparison with the results for the $^2E''$ basis set, calculated with $k = 1.0$, shows a lowering of the magnetic moment of *ca.* 0.05 BM at room temperature with the difference falling at lower temperatures.

Also included in Figure 4 are plots showing the variation of moment for two different values of the parameter k calculated using the zero-order eigenfunctions. Here too, we find a lowering of the magnetic moment toward the spin-only value and toward the observed behavior. However, if we take 0.6 as a
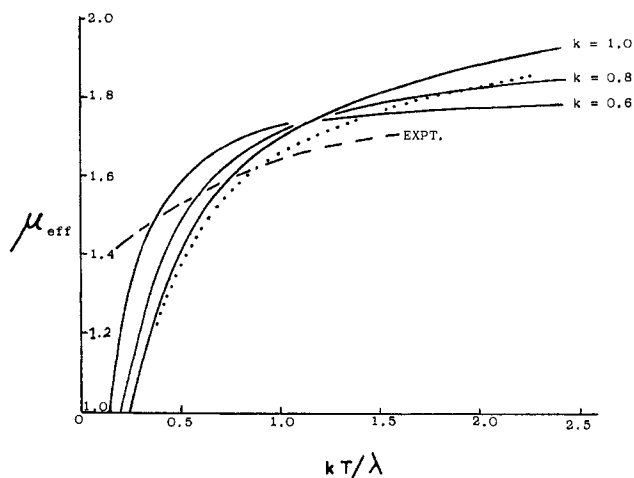

Figure 4.—μ_{eff} *vs.* kT/λ for the $^2E''$ term calculated including electron delocalization (full lines) and using the first-order corrected eigenfunctions (dotted line). The experimental variation is also indicated (broken line).

lower limit for the (isotropic) orbital reduction factor[24] and also use the ^2D basis functions, we can only approximate the experimental results at higher temperatures, the low-temperature data, as noted above, indicating the presence of a low-symmetry ligand field component.

The presence of a lower symmetry ligand field than D_{3h} is even more evident in the case of the chromium complex $CrCl_3 \cdot 2N(CH_3)_3$, the observed spin-only behavior over a large temperature range, as indicated by Table I, being indicative of an orbital singlet as ground state and being very different from the behavior predicted by the expression in Table III and illustrated in Figure 3. In fact, a large deviation from D_{3h} symmetry in this complex was predicted on the basis of its electronic spectra, while no similar conclusion could be drawn in the case of the titanium species.[4]

(2) Magnetic Properties for C_{2v} Symmetry.—Removal of the orbital degeneracy of the E' and E'' states is brought about by destroying the threefold symmetry, i.e., the variation of the equatorial bond angle from $2\pi/3$, and this is the distortion from D_{3h} symmetry observed in the $TiBr_3 \cdot 2N(CH_3)_3$ and $CrCl_3 \cdot 2N(CH_3)_3$ molecules, the symmetry of the polyhedra being C_{2v}. The lowest energy orbital is therefore d_{zz} or d_{yz}, dependent on the labeling of axes.

Since for the titanium complexes, the additional low-symmetry ligand field component is probably small, its operation must be discussed with reference to the spin–orbit coupling constant and to kT.

Denoting the splitting of the $^2E''$ ground state (or the e'' orbitals) by Δ, the eigenfunctions for the two resulting levels are clearly $2^{-1/2}[|1\rangle + |-1\rangle]$, ϕ_1, and $2^{-1/2}[|1\rangle - |-1\rangle]$, ϕ_2, each with spin states α and

(21) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1965).
(22) B. N. Figgis, *Trans. Faraday Soc.*, **57**, 198 (1961).
(23) See ref 15 and 15a in ref 4. Also see P. C. Crouch, G. W. A. Fowles, and R. A. Walton, *J. Chem. Soc., A*, in press.

(24) For systems lacking an inversion center, such as that treated here, values for k somewhat lower than those usually found in octahedral systems seem possible. In D_{3h} symmetry the $4p_z$ and $4p_y$ orbitals also transform as e'', so that "mixing" with the 3d orbitals can "aid" delocalization and hence lead to a relatively lower value of k.

β. Inclusion of spin–orbit coupling leads to an energy separation for the two Kramers doublets of $(\Delta^2 + \lambda^2)^{1/2}$, the relevant wave functions for the two doublets being linear combinations of ϕ_1 and ϕ_2 with the same spin. Operating with $\mathbf{u}_{||}$ and $\mathbf{u}_{\perp}$ one now finds first- and second-order Zeeman energies for both orientations of H. The variation of magnetic moment with kT/λ as derived from these energies is illustrated in Figure 5 as a function of the ratio of Δ/λ. It is seen from these plots that the most marked effect of the introduction of a small distortion occurs at lower temperatures and that for a small splitting of the $^2E''$ state of 300 cm^{-1} ($\Delta/\lambda = 2$) the magnetic moment is greater than the observed values of both chloride and bromide complexes. The Δ value of 300 cm^{-1} can then be considered as the approximate upper limit to the splitting of the $^2E''$ state since any electron delocalization will also increase the calculated magnetic moment at low temperatures.

So far neglected in the preceding discussion are TIP contributions to the experimental susceptibility, which arise from the "mixing" (in D_{3h}) of the $^2E'$ state with $^2E''$ via $\mathbf{u}_{\perp}$. While this is relatively small for the titanium complexes (amounting to *ca.* 140×10^{-6} cgsu), it is important, as making allowance for it leads to a room temperature μ_{eff} of 1.60 BM.

In summary, therefore, we can conclude that a discussion of the magnetic data for the d^1 configuration over a relatively wide temperature range must involve at least use of the "complete" basis set, orbital reduction, and also a small low-symmetry ligand field component. We have neglected any consideration of interaction between neighboring molecules in the crystal, since the structure analysis shows the metal atoms to be well separated.

Considering the chromium complex, to obtain an approximate estimate of the low-symmetry ligand field component operative here, *i.e.*, the splitting of the $^4E'$ state, we can follow the same method as for the d^1 configuration. While in D_{3h} the wave functions with $M_L = \pm 2$ form a basis for E', in C_{2v} symmetry
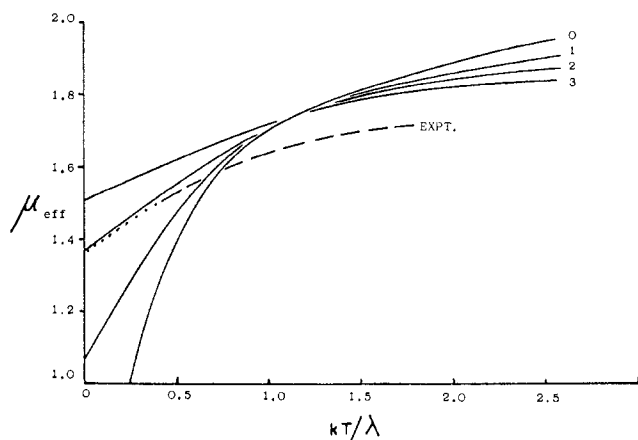
the appropriate wave functions for the two levels, again denoting their separation by Δ, are easily seen to be $2^{-1/2}[|2\rangle + |-2\rangle]$, ϕ_1, and $2^{-1/2}[|2\rangle - |-2\rangle]$, ϕ_2, each with M_S values $^3/_2$ through $-^3/_2$. Inclusion of first-order spin–orbit coupling splits the fourfold degenerate states into two pairs of Kramers doublets with energies $\pm [(3\lambda)^2 + (\Delta/2)^2]^{1/2}$ and $\pm [\lambda^2 + (\Delta/2)^2]^{1/2}$. The relevant eigenfunctions for these doublets can be written as linear combinations of ϕ_1 and ϕ_2 with relevant M_S values, as before.

The variation of μ_{eff} with kT/λ calculated from these eigenfunctions, for two values of the parameter Δ, is illustrated in Figure 6. It appears that a much larger low-symmetry ligand field component is needed to produce a spin-only magnetic moment for the $^4E'$ term than in the case of the d^1 configuration. Although no correction has been made to the observed data for TIP terms (which will probably be negligible in view of the high molar susceptibility) or for orbital delocalization, it appears that the splitting of the $^4E'$ ground state in $CrCl_3 \cdot 2N(CH_3)_3$ must be at least 2000 cm^{-1} in order to give rise to the observed (virtually) temperature-independent spin-only moment. The relative magnitudes of Δ for the titanium and chromium complexes are therefore in keeping with the observed distortions of the coordination polyhedra from D_{3h} geometry; *i.e.*, $CrCl_3 \cdot 2N(CH_3)_3$ is more distorted, although no quantitative correlation is in fact possible, since we cannot readily relate Δ for the chromium complex to the orbital energy separation between d_{zz} and d_{yz}.

(3) Complexes of C_{3v} Symmetry.—Detailed evaluation of the predicted magnetic properties for this symmetry would be a tedious undertaking since crystal field states, belonging to different representations in D_{3h}, now belong to the same representation in C_{3v} and
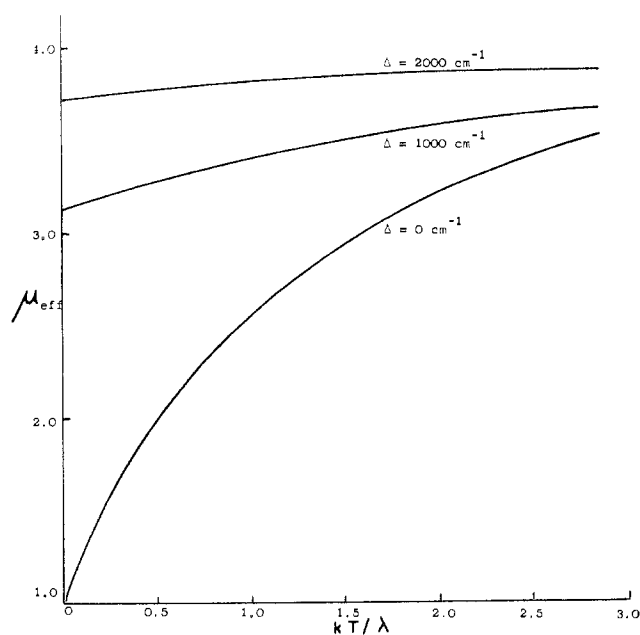

Figure 5.—μ_{eff} *vs.* kT/λ for the $^2E''$ term in the presence of a ligand field component of low symmetry (in the equatorial plane). The numbers attached give the ratio Δ/λ.

Figure 6.—μ_{eff} *vs.* kT/λ for the $^4E'$ term including a low-symmetry ligand field component of varying magnitude.

can "mix" together.[4] In any event, the paucity of experimental data does not warrant such an evaluation and a qualitative consideration will suffice.

Only a room-temperature measurement is available for the iron complexes $Fe(Me_6tren)X^+$ ($X = Cl$, Br),[10] and this value, namely, 5.34 BM, comes very close to that predicted for the $^5E''$ term (Figure 3), *viz.*, 5.27 BM. In C_{3v} symmetry, the ground state $^5E(1)$ contains a certain proportion of the eigenfunction with $M_L = \pm 2$. Since the E'' term eigenfunctions have $M_L = \pm 1$, the inclusion of the higher energy term in C_{3v} symmetry might be expected to lead to a higher magnetic moment than for $^5E''$ in D_{3h}. The observed increase for the iron complexes is however barely significant.

In the case of the nickel complex $Ni(Me_6tren)Cl^+$, the magnetic moments at three temperatures have been determined,[11] and these are 3.48 BM (79°K), 3.52 BM (192°K), and 3.42 BM (295°K). These values are much lower than would be predicted by the $^3E'$ ground state for D_{3h} symmetry (which is given in Figure 3), although the form of the temperature variation is approximately the same. The lower values for C_{3v} symmetry can be rationalized by noting that the excited states of E symmetry, previously E'' in D_{3h}, and arising from ^3F and ^3P, which can now be "mixed" into the ground state, are eigenfunctions with $M_L = \pm 1$, while the ground-state eigenfunctions have $M_L = \pm 2$. The corresponding bromide complex has recently been shown by X-ray analysis to contain a polyhedron with C_{3v} symmetry,[25] so that any deviation of the moment from that predicted cannot be due to removal of orbital degeneracy and must be a result of lowering the symmetry from D_{3h}. It will be shown in a further paper that the corresponding cobalt complexes, $Co(Me_6tren)X^+$, have magnetic moments greater than would be predicted from a D_{3h} model.

Conclusions and Summary

The magnetic properties anticipated for pentacoordinate molecules of D_{3h} symmetry and having orbitally degenerate ground states have been considered in detail and the variation of μ_{eff} with kT/λ for weak crystal field terms is given. In the case of the $^2E''$ and $^5E''$ terms this variation is very similar to that

anticipated for the $^2T_{2g}$ and $^5T_{2g}$ octahedral terms.

From the study of the magnetic moments of the trimethylamine adducts of the titanium and chromium trihalides, over a temperature range, it appears that, in common with octahedral and tetrahedral species which theoretically have orbitally degenerate ground states in the absence of spin–orbit coupling, the magnetic properties of these pentacoordinate molecules differ markedly from those predicted and tend toward the appropriate spin-only value. While the orbital degeneracy of the E terms can be removed by spin–orbit coupling, as is true for T_1 and T_2 terms, this mechanism is insufficient to lift the degeneracy completely, and hence a lower symmetry ligand field than D_{3h} is necessary. Rough assessment of the magnitude of the distortion present, as measured by the splitting of the orbitally degenerate ground state, is in keeping with the simple picture one has of the Jahn–Teller effect; *i.e.*, for the d^1 configuration, the electron is located in e'' nonbonding orbitals, so that any deviation from D_{3h} should be smaller than with the odd electron in the e' orbitals, as for d^3. This is the order of the deviation found from the results of X-ray structure analyses. Since the series of trimethylamine adducts of TiX_3, VX_3, $VOCl_2$, and $CrCl_3$ are isomorphous and virtually isostructural in the solid state, it is then reasonable to attribute the finer details of the stereochemistry to the number of d electrons in the metal ion.

More detailed study of the d^1 configuration would include simultaneous variation of the orbital reduction factor, spin–orbit coupling constant, and low-symmetry ligand field component, but in the absence of single-crystal data, it is doubtful if there would be a unique fit for these three parameters. However, the above results illustrate the relevance of these factors in "explaining" the detailed magnetic properties of the titanium species and moreover stress the importance of using the first-order corrected eigenfunctions as the basis set.

In summary then, it appears that much of the detailed theory and ideas applied to the description of the magnetic properties of cubic and quasi-cubic systems can be applied equally well to five-coordinate molecules.

(25) M. Di Vaira and P. L. Orioli, *Acta Cryst.*, **24B**, 595 (1968).