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THE EFFECT OF AXIAL LIGAND FIELDS ON GROUND STATE PROPERTIES OF COMPLEXES WITH ORBITALLY DEGENERATE GROUND TERMS

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CONTENTS

ABBREVIATIONS

acac	= acetylacetonate	opd	= *o*-phenylenediamine
dipy	= $\alpha\alpha'$ dipyridyl	diars	= *o*-phenylenebisdimethylarsine
phen	= 1:10 phenanthroline	THF	= tetrahydrofuran
en	= ethylenediamine	DTC	= dithiocarbonate
py	= pyridine	Quin H	= (Quinolinium)$^+$
pic	= picoline	PQ	= (*NN'*-dimethyl-44'-dipyridyl)$^{2+}$
IQ	= isoquinoline	Cat	= [$\alpha\alpha'$-(bis-triphenylphosphonium)*p*-xylene]$^{2+}$

A. INTRODUCTION

During the 1930's the crystal field description of the electronic and magnetic properties of co-ordinated transition metal ions was developed by physicists[1,2,3]. The electrostatic field produced at the site of the metal ion was generally assumed to have cubic symmetry, altnough Schlapp and Penney considered the additional effect of an orthorhombic potential in their calculations[2].

In recent years new theoretical and experimental ideas have revealed the inadequacies of this simple theory. Now it is widely accepted that the electric and magnetic properties of transition metal complexes are more aptly described by a ligand field model incorporating non-cubic potential operators. Recent review articles have discussed the effects of covalent bonding[4], and the splitting of excited terms as observed in the electronic spectra of metal complexes[5]. It is the purpose of this article to review the effects of non-cubic ligand fields on the ground terms of transition metal ions and to discuss some of the experimental results which have revealed the presence of these fields.

B. THEORY

(i) General remarks

Most transition metal complexes show the effects of distortion produced by non-cubic ligand fields in their ground terms, their excited terms or in both. Non-cubic fields may arise as a consequence of (a) the presence of dissimilar ligands, *e.g.* MA_4B_2 complexes, (b) packing distortions produced by the presence of ions of different sizes, (c) the Jahn–Teller effect, where (b) and (c) are probably inseparable.

Axial distortions are commonly described by the irreducible representations of the D_{4h} or C_{4v} point groups in the tetragonal case and by those of either the D_{3d} or C_{3v} point groups in the case of a trigonal distortion. The lower symmetry rhombic field corresponds to the point group D_{2d}. The orbital and term splitting that arises by descending in symmetry from an octahedral to an axial environment is given by:

O_h	→	D_{4h}	→	D_{3d}
A_{1g}		A_{1g}		A_{1g}
A_{2g}		B_{1g}		A_{2g}
E_g		$A_{1g}+B_{1g}$		E_g
T_{1g}		$A_{2g}+E_g$		$A_{2g}+E_g$
T_{2g}		$B_{2g}+E_g$		$A_{1g}+E_g$

To a first order approximation the effect of an axial ligand field component will only be felt by those complexes which exhibit the orbitally degenerate terms E_g,

T_{1g} and T_{2g} in a cubic field. Consequently we shall only be concerned with metal ions that have orbitally degenerate ground terms in cubic symmetry. The case of rhombic symmetry is more complicated than axial symmetry and since the majority of complexes may be considered on the basis of an axial distortion plus spin-orbit coupling we shall not be concerned with rhombic distortions. Since confusion between tetrahedral and octahedral symmetry is unlikely to arise we shall omit the subscript g on all symmetry labels. Much of the experimental data to be discussed is derived from magnetic measurements, now Eg terms comprise a "non-magnetic" doublet in cubic symmetry consequently complexes with T_1 or T_2 ground terms are dealt with most numerously. These terms arise from the following metal ion configurations: $^5T_2$ from d^6 octahedral and d^4 tetrahedral, $^4T_1$ from d^7 octahedral and d^3 tetrahedral, $^3T_1$ from d^2 octahedral, d^8 tetrahedral and d^4 spin-paired octahedral and $^2T_2$ from d^1 octahedral, d^9 tetrahedral and d^5 spin-paired octahedral.

Although the application of group theory provides a facile means of deciding when a cubic field representation will be reduced by a non-cubic environment, it does not permit us to estimate either the sign or the magnitude of the ensuing separation of energy levels. Several calculations have been reported in which an axial perturbation is added to the cubic field potential. Since we are not primarily concerned with covalency effects we will not develop the ligand field approach[5–7] but will concentrate on the point-charge or point-dipole model[8–16].

(ii) Models used to describe axial field effects

Axial fields are usually treated as perturbations, in the absence of spin-orbit coupling, upon the cubic field eigenfunctions[13]. The arguments applying to the tetragonal and trigonal field cases are similar hence only the former is discussed here. For a tetragonally distorted system the total crystalline field potential is given by:

$$V = aY_2^0 + bY_4^0 + c(Y_4^4 + Y_4^{-4}), \tag{1}$$

and the cubic field potential $V_0 = Y_4{}^0 + \sqrt{\frac{5}{14}}\,(Y_4{}^4 + Y_4{}^{-4})$ (2)

Where a, b and care constants to be determined and the Y_l^m are Tesseral harmonics. By assuming that the tetragonal perturbation does not disturb the orbitals in the xy plane[13], c = $\sqrt{\frac{5}{14}}$ and

$$V = {}_0 + V_T \tag{3}$$

where

$$V_T = aY_2^0 + b'Y_4^0 \tag{4}$$

In order to evaluate the matrix elements of the axial perturbation, V_T is expressed in operator form,

$$V_T = Ds(l_z^2 - 2) - Dt\left(\frac{35}{12}l_z^4 - \frac{155}{12}l_z^2 + 6\right) \tag{5}$$

where Ds and Dt are the axial field splitting parameters for Y_2^0 and Y_4^0 respectively, corresponding to Dq in the cubic field case.

The single parameter axial field model[14] assumes that b' = 0 in (4) and $Dt = 0$ in (5), such that the tetragonal field is due solely to the term aY_2^0. In contrast the two parameter axial field model[8] considers the more general case with from zero b' being different, which appears to be necessary for a discussion of the excited states of a molecule[5,16–20]. Ground state properties such as the magnetic moment[14] and the quadrupole splitting in the Mössbauer spectrum[21,22] have been accounted for on the basis of the single parameter model, hence we shall concentrate on this model.

The non-zero matrix elements of V_T for the one electron d eigenfunctions in a weak primary field assuming that $Dt = 0$ are given by equation (6).

$$\begin{aligned} \langle \pm 2 \mid V_T \mid \pm 2 \rangle &= 2Ds \\ \langle \pm 1 \mid V_T \mid \pm 1 \rangle &= -Ds \\ \langle 0 \mid V_T \mid 0 \rangle &= -2Ds \end{aligned} \tag{6}$$

The effect of the axial field on the spectroscopic terms of complexed metal ions are derived from (6) by taking the necessary linear combinations of the one electron eigenfunctions required to describe the various terms. If we define the separation between the split ground term orbital components to be Δ, and let Δ be

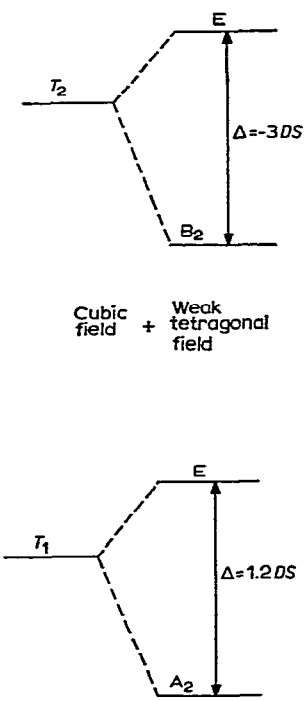

Fig. 1. Splitting of T_1 and T_2 terms in a weak tetragonal field with Δ positive.

positive when the orbital singlet lies below the orbital doublet, as in Fig. 1, then for $^5T_2$ and $^2T_2$ terms $\Delta = -3Ds$. For $^4T_1$ and $^3T_1$ terms in a weak field $\Delta = 1{,}2Ds$ and in a strong field $\Delta = 3Ds$.

In the case of a trigonal potential acting on a weak primary field the non-zero matrix elements of V_T for the one electron d eigenfunctions are again given by equation (6) for the single parameter axial field model. This gives, for $^5T_2$ and $^2T_2$ terms, $\Delta = 3Ds$, and for $^4T_1$ and $^3T_1$ terms in a weak field $\Delta = -0{,}3Ds$ and in a strong field $\Delta = -3Ds$. These estimated values of Δ are related to the physical deformation of an octahedron or a tetrahedron by letting Ze be the charge on the ligands, $\bar{r}^2$ be the mean square distance of the d electron from the metal nucleus, a be the metal–ligand separation for the 4 in-plane ligands, b be the metal–ligand separation for the two ligands on the opposite sides of this plane and α be the angle subtended at the metal ion by a vertex and the c_4 axis[14]. Then for a tetragonal distortion of an octahedron

$$Ds = \frac{2}{7} Ze\bar{r}^2 \left(\frac{1}{b^3} - \frac{1}{a^3} \right) \tag{7}$$

so that Ds is negative for a compression along the C_4 axis since Ze is a negative quantity and $b < a$. Conversely Ds is positive for an extension along the C_4 axis. For an octahedron deformed along a trigonal axis

$$Ds = \frac{3}{7} \frac{Ze\bar{r}^2}{a^3} (1 - 3\cos^2 \alpha) \tag{8}$$

so that Ds is positive for a compression and negative for an extension along the trigonal axis. Hence for an octahedron distorted by either a tetragonal or a trigonal deformation a compression along the major symmetry axis produces a positive value of Δ for T_2 terms and a negative value for T_1 terms.

In the case of a tetrahedron with a tetragonal distortion along the S_4 axis

$$Ds = \frac{Ze\bar{r}^2}{a^3} (1 - 3\cos^2 \alpha) \tag{9}$$

which implies that Ds is positive for a compression of the tetrahedron and negative for an elongation along the tetragonal axis. When a tetrahedron is distorted along a three-fold symmetry axis Ds is positive for the deformation that corresponds to the ligands being forced away from the three-fold axis to give C_{3v} symmetry.

In general the sign of Δ produced by distortion of a tetrahedron is opposite to that produced by a similar distortion of an octahedron. These theoretical predictions of the splitting of triply degenerate ground terms in transition metal complexes are not yet extensively tested due to a paucity of sufficiently accurate experimental data[14].

The Jahn–Teller Theorem allows us to predict that any molecule with an orbitally degenerate ground term will be distorted such that an orbital singlet lies lowest corresponding to a positive value of Δ[23]. Several reports have been made

of the attempted *ab initio* calculation of the distortion expected from this source but they appear not to be very successful[24–26]. Estimates of Δ from electronic spectra have suggested values of the order of a few thousand cm^{-1}, which implies that the axial field energy is comparable to that of spin-orbit coupling and thermal effects. When we consider ways of estimating Δ for a ground term these other effects must also be taken into account.

C. BACKGROUND TO EXPERIMENTAL MEASUREMENTS OF AXIAL FIELDS

If the sample is available as a well classified single crystal then much more information is potentially available than if the sample is polycrystalline. In practice polycrystalline materials are much more common than good single crystals so that we will deal with parameters suitable for interpreting data for the former case and mention the necessary extensions of the theory to the latter where appropriate.

(i) Magnetic susceptibilities

Van Vleck[27] has expressed the energy E_i corresponding to the wavefunction ψ_i, as a power series in the applied magnetic field H.

$$E_i = E_i^0 + E_i^{I}H + E_i^{II}H^2 + \ldots\ldots\ldots \tag{10}$$

where E_i^0 is the energy of the unperturbed state, E_i^{I} is the first order Zeeman coefficient $= \langle\psi_i \mid \hat{\mu}_z \mid \psi_i\rangle$ and E_i^{II} is the second order Zeeman coefficient

$$= \sum_j \frac{(\langle\psi_i \mid \hat{\mu}_z \mid \psi_j\rangle)^2}{E_i^0 - E_j^0}, \quad i \neq j. \tag{11}$$

The z component of the magnetic moment operator $\hat{\mu}_z = (\hat{L}_z + 2\hat{S}_z)\beta$, where L_z and $\hat{S}_z$ are the orbital and spin angular momentum operators in the z direction, and β is the Bohr Magneton; similar expressions exist for the x and y components. In a cubic environment the magnetic moment is isotropic so that the x, y and z components of the Zeeman coefficients are equal. For non-cubic symmetry the magnetic moment becomes anisotropic and the first and second order Zeeman coefficients must be evaluated individually for each direction. The resulting energy of the system is dependent upon the Boltzmann distribution among the energy levels described by the operators relevant to the cubic and non-cubic crystalline field potentials, the spin-orbit coupling and the applied magnetic field. The mean energy is E_α where

$$E_\alpha = \frac{\sum_i E_{i_\alpha} e^{\frac{-E_{i_\alpha}}{kT}}}{\sum_i e^{\frac{-Ei_\alpha}{kT}}}$$

$\alpha = x, y$, or z in the general case or $\perp$, $\parallel$ in the case of axial symmetry. The susceptibility x of the system is related to the mean energy by

$$\mathrm{X}_{\alpha} = \frac{1}{H}\left(\frac{\partial E_{\alpha}}{\partial H}\right) \tag{13}$$

which gives the following expression for the molar susceptibility $\mathrm{x_M}$

$$\mathrm{X}_{\alpha\mathrm{M}} = \frac{N \sum_{\mathrm{i}} \left[\frac{(E^{\mathrm{I}}_{\mathrm{i}_\alpha})^2}{kT} - 2\,E^{\mathrm{II}}_{\mathrm{i}_\alpha \mathrm{i}_\alpha}\right] \mathrm{e}^{\frac{-E^0_{\mathrm{i}_\alpha}}{kT}}}{\sum_{\mathrm{i}} \mathrm{e}^{\frac{-E^0_{\mathrm{i}_\alpha}}{kT}}} \tag{14}$$

The magnetic moment P being related to the molar susceptibility by

$$P_{\alpha} = 2{,}828\,(\mathrm{X}_{\alpha\mathrm{M}}T)^{\frac{1}{2}} \tag{15}$$

It is apparent from equations (14) and (15) that the molar susceptibility and hence the magnetic moment at a given temperature is dependent upon which energy levels of the system are occupied and this in turn depends largely upon the effects of spin-orbit coupling and the non-cubic field potential. The case in which the axial field potential is much more effective than spin-orbit coupling in raising the orbital degeneracy has been discussed in general terms[28] by taking expressions for the g tensor to derive expressions for the magnetic moment, see page 122.

Before evaluating the matrix elements of the Zeeman coefficients in (14) it is necessary to consider two further parameters k and A. k describes the reduction in the orbital angular momentum of the free-atom eigenfunctions due to electron delocalisation[29], it is defined by

$$k_{\mathrm{ij}} = \frac{\langle \psi_{\mathrm{i}} \mid \hat{\mathrm{L}} \mid \psi_{\mathrm{j}} \rangle}{\langle \phi_{\mathrm{i}} \mid \hat{\mathrm{L}} \mid \phi_{\mathrm{j}} \rangle} \tag{16}$$

where ψ denotes a molecular orbital of the complex and ϕ an atomic orbital of the free metal ion. The parameter A accounts for the enhancement of the orbital angular momentum of the ground term by interaction with an excited term. This is of importance when a T_1 term from a free ion F term lies lowest since lying closely above it is a second T_1 term from a free ion P term. The amount of interaction between these two T_1 terms depends upon the strength of the crystalline field, A varies from 1,5 in a weak field to 1,0 in a strong field[30]. For a given complex its value may be determined from electronic spectroscopic data. Including k and A the following expressions are obtained for the major components of the magnetic moment operator in axial symmetry

$$\hat{\mu}_{\parallel} = (k_{\parallel}A_{\parallel}\hat{L}_z + 2\hat{S}_z)\beta \tag{17}$$

and

$$\hat{\mu}_{\perp} = (\tfrac{1}{2}k_{\perp}A_{\perp}(\hat{L}_- + \hat{L}_+) + \hat{S}_- + \hat{S}_+)\,\beta$$

where

$$\hat{L}_{\pm} = \hat{L}_x \pm i\hat{L}_y \text{ and } \hat{S}_{\pm} = \hat{S}_x \pm i\hat{S}_y$$

For metals from the first transition series the effect of the axial field Δ and the spin-orbit coupling λ are of the same order of magnitude. Hence the perturbations due to Δ and λ have to be treated simultaneously and each case has to be considered individually as discussed in section D. The theoretical arguments used to evaluate the matrix elements in each case usually involve the following assumptions:

(a) Spin-orbit coupling matrix elements between T_1 and T_2 terms with the same spin multiplicity are ignored. In practice this could sometimes produce an additional splitting of a few cm^{-1}.

(b) $\Delta \ll 10\,Dq$ so that the off-diagonal matrix elements of the axial potential between the ground term and the higher terms with E symmetry may be neglected.

(c) The departure from cubic symmetry is described by an axial field component which has the same axes as the cubic field potential.

(d) The parameters λ k and Δ are taken to be isotropic.

In general unless $\Delta > \lambda$ the effect of the axial field upon the average magnetic susceptibility is not large but the components $\chi_{\parallel}$ and $\chi_{\perp}$ are very much more sensitive to the presence of an axial field environment. Therefore more reliable estimates of Δ are available from single crystal measurements than from average susceptibilities which in some cases cannot be fitted unambiguously to the theoretical data.

The magnetic properties of a crystal are usually measured by means of the 3 orthogonal principal crystal susceptibilities S_1, S_2, S_3. These are defined by the three directions in which the crystal is in stable mechanical equilibrium when placed in a magnetic field. For a crystal with high symmetry (cubic, tetragonal, trigonal, orthorhombic or hexagonal) the directions in which S_1, S_2, S_3 are measured are the crystal axes a, b and c. Usually S_3 lies along b, the major symmetry axis of the crystal, and $S_1 > S_2$.

If the crystal is monoclinic then S_3 is measured along the b axis, and S_1 and S_2 in the ac plane where they make angles θ and ϕ with the a and c axes.

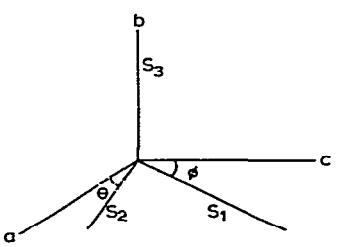

Fig. 2. The directional relationship between the principle crystal susceptibilities S_1, S_2 and S_3 and the crystal axes a, b and c.

Under these conditions

$$S_b = S_3$$
$$S_a = S_1 \sin^2\theta + S_2 \cos^2\theta \quad (18)$$

and

$$S_c = S_1 \cos^2\phi + S_2 \sin^2\phi .$$

In the case of a triclinic crystal none of the principal susceptibilities of the crystal may correspond with a given crystal axis and each case must be considered individually.

Having discussed the susceptibilities of the crystal we must now consider how to relate them to the three[31] orthogonal molecular susceptibilities x_1, x_2 and x_3. If the direction cosines between x_1 and S_1, S_2 S_3 for the nth molecule in the unit cell are k_{1n}, l_{1n} and m_{1n} with similar expressions for the x_2 and x_3 direction cosines then,

$$S_1 = \sum_n X_1 k_{1n}^2 + X_2 k_{2n}^2 + X_3 k_{3n}^2$$
$$S_2 = \sum_n X_1 l_{1n}^2 + X_2 l_{2n}^2 + X_3 l_{3n}^2 \quad (19)$$

and

$$S_3 = \sum_n X_1 m_{1n}^2 + X_2 m_{2n}^2 + X_3 m_{3n}^2$$

where the summation is over all of the molecules in the unit cell. If the x values are to be expressed as molai susceptibilities then the left hand side of equation (19) should be multiplied by the molecular weight.

As an example consider the case of a metal ion in a crystal field environment of D_{4h} symmetry in a monoclinic crystal. Then $x_1 = x_2 = x_\perp$ and $x_3 = x_\parallel$. Let α be the angle between the z axis of the octahedron of ligand atoms and the ac plane of the crystal. If Δ is positive then $x_\perp > x_\parallel$ and since by convention $S_1 > S_2$ we have

$$S_1 = X_\perp$$
$$S_2 = X_\parallel \cos^2\alpha + X_1 \sin^2\alpha$$
$$S_3 = X_\parallel \sin^2\alpha + X_1 \cos^2\alpha \quad (20)$$

Therefore $X_1 = S_1$

and $$X_\parallel = S_3 + S_2 - S_1 \quad (21)$$

If Δ negative then $x_\parallel > x_\perp$ and S_1 and S_2 are interchanged. Hence by experimentally measuring S_1, S_2 and S_3, $x_\parallel$ and $x_\perp$ are found which are related to particular values of λ and Δ.

(ii) Mössbauer effect[32]

The transition metal nucleus most widely studied by the Mössbauer effect is ^{57}Fe. It has a first excited nuclear spin level with spin quantum number I = 3/2

which lies 14,4 KeV (1 KeV = $8{,}07 \times 10^6$ cm^{-1}) above the ground level which has I = 1/2. A Mössbauer spectrum is produced by the recoiless absorption or emission of a γ ray, resulting in a transition between these nuclear spin levels. All nuclear spin levels with $I \geq 1$ have a quadrupole moment associated with them. In the case of the first excited level of ^{57}Fe the quadrupole moment will interact with an extranuclear electric field gradient to produce a degenerate pair of states $I_z = \pm 3/2$ at a different energy from the other degenerate pair $I_z = \pm 1/2$. This is expressed by the Hamiltonian operator $\hat{H}_Q$[33]

$$\hat{H}_Q = \frac{eQ}{4I(2I-1)}[V_{zz}(3I_z^2 - I(I+1)) + (V_{xx} - V_{yy})(I_x^2 - I_y^2)] \tag{22}$$

Where V_{xx}, V_{yy} and V_{zz} are the components of the electric field gradient tensor at the nucleus, and eQ is the nuclear quadrupole moment. If we assume axial symmetry then $V_{xx} = V_{yy}$ and $V_{zz} = eq$, under these conditions we can write H_Q as,

$$\hat{H}_Q = \frac{eqeQ}{4I(2I-1)}[3I_z^2 - I(I+1)] \tag{23}$$

Since $\hat{H}_Q$ is a minor component of the total Hamiltonian of the system we need only consider the diagonal matrix elements in order to find E_Q the interaction between the quadrupole moment and the electric field gradient.

$$E_Q = \langle I, I_z \mid \hat{H}_Q \mid I, I_z \rangle \tag{24}$$

From (23) and (24) it is apparent that when $I = 1/2$ and $I_z = \pm 1/2$, $E_Q = 0$. When $I = 3/2$ and $I_z = \pm 1/2$, $E_Q = -e^2qQ/4$ and when $I = 3/2$ and $I_z = \pm 3/2$, $E_Q = e^2qQ/4$. So that the nuclear spin ground level of ^{57}Fe is unsplit whilst the first excited level is split into 2 degenerate sets of states by $E_Q = e^2qQ/2$. As shown in Fig. 3 the Mössbauer spectrum now consists of two lines whose separation ΔE_Q

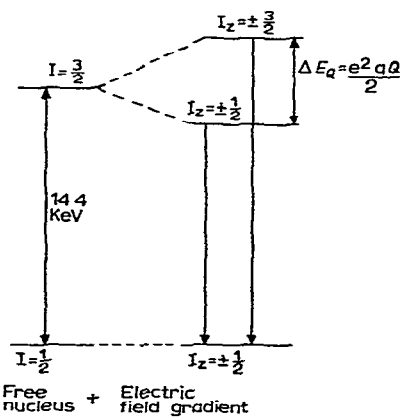

Fig. 3. Quadrupole splitting produced in the Mössbauer spectrum of an ^{57}Fe nucleus by an electric field gradient.

depends upon the nuclear parameter eQ, which is constant for a given nuclear spin level, and the electronic parameter eq. The actual field gradient that the nucleus experiences depends upon the electronic configuration of the transition metal ion because the expectation value of q, written as $\langle q \rangle$, is not the same for each of the d orbitals. Ingalls[22,34] has shown that there are two major contributions to q which are expressed by $q_{val.}$ and $q_{lat.}$. These account for the field gradient produced by the valence electrons and the lattice charge distribution respectively. For an axial environment

$$q = q_{val.}(1-R)+q_{lat.}(1-\gamma) \tag{25}$$

where $(1-R)$ and $(1-\gamma)$ are the Sternheimer factors which are included to correct for the polarisation of the d electron core by the terms $q_{val.}$ and $q_{lat.}$.

Now

$$\langle q_{val} \rangle_i = \left\langle \frac{V_{zz}}{e} \right\rangle_i \tag{26}$$

where (26) applies for each of the i occupied d orbitals. By using the single parameter axial field model we get,

$$\left\langle \frac{V_{zz}}{e} \right\rangle_i = -\left\langle \frac{3z^2-r^2}{r^5} \right\rangle_i \tag{27}$$

Bleaney and Stevens[35] have shown that

$$\langle 3z^2-r^2 \rangle_i = \alpha \langle r^2 \rangle_i [3L_z^2-L(L+1)] \tag{28}$$

Where $\langle r^2 \rangle_i$ refers to the expectation value of the square of the radius of the ith d orbital, and $\alpha = -\frac{2}{21}$ for the configurations $3d^1$ and spin-free $3d^6$.

Therefore

$$\left\langle \frac{V_{zz}}{e} \right\rangle_i = \frac{2}{21} \langle r^{-3} \rangle_i [3L_z^2-L(L+1)] \tag{29}$$

By using the usual combinations of one-electron wavefunctions (29) is evaluated to give the following values for

$\left\langle \frac{V_{zz}}{e} \right\rangle$:

$\frac{-4}{7} \langle r^{-3} \rangle$ for the d_z^2 orbital

$\frac{-2}{7} \langle r^{-3} \rangle$ for the dxz and dyz orbitals (30)

and

$\frac{4}{7} \langle r^{-3} \rangle$ for the dxy and dx^2-y^2 orbitals

assuming that the radii of each member of the set of $3d$ orbitals are equal. By a similar argument for an axial field splitting Δ of the lowest orbital triplet,

$$\langle q_{lat} \rangle = \frac{-14\Delta}{3e^2} \langle r^{-2} \rangle \tag{31}$$

Assuming that the quadrupole precession times ($\sim 10^{-8}$ sec) are very much longer than the thermal transition times between the orbital triplet levels (10^{-9}–10^{-11} sec) the effective field gradient will be an average of the contributions of the three levels each weighted by the appropriate Boltzmann factor. When the axial field splitting produces the *dxy* orbital lying lowest Δ is positive[20] and

$$q_{val.} = \frac{4}{7} \langle r^{-3} \rangle \frac{\left(1 - e \frac{-\Delta}{kT}\right)}{\left(1 + 2e \frac{-\Delta}{kT}\right)} \tag{32}$$

By substituting (31) and (32) into (25) we get

$$q = \frac{4}{7} \langle r^{-3} \rangle (1 - R) \frac{\left(1 - e \frac{-\Delta}{kT}\right)}{\left(1 + 2e \frac{-\Delta}{kT}\right)} - \frac{14\Delta}{3e^2} \langle r^{-2} \rangle (1 - \gamma) \tag{33}$$

and

$$\Delta E_Q = \frac{e^2 Q}{2} \left[\frac{4}{7} \langle r^{-3} \rangle (1 - R) \frac{\left(1 - e \frac{-\Delta}{kT}\right)}{\left(1 + 2e \frac{-\Delta}{kT}\right)} - \frac{14\Delta}{3e^2} \langle r^{-2} \rangle (1 - \gamma) \right] \tag{34}$$

If the axial field produces a negative value of Δ with the *dxz*, *dyz* orbitals lying lowest, then

$$\Delta E_Q = \frac{-e^2 Q}{2} \left[\frac{4}{7} \langle r^{-3} \rangle (1 - R) \frac{\left(1 - e \frac{-\Delta}{kT}\right)}{\left(2 + e \frac{-\Delta}{kT}\right)} - \frac{14\Delta}{3e^2} \langle r^{-2} \rangle (1 - \gamma) \right] \tag{35}$$

By measuring the quadrupole splitting ΔE_Q as a function of temperature we are able by the use of (34) and (35) to estimate a value for the axial splitting parameter Δ. By including the effects of spin-orbit coupling and covalency, the value of ΔE_Q is slightly reduced for comparable values[22] of Δ and λ, but the general variation of ΔE_Q as a function of Δ is almost unchanged[20]. Due to the similarity of equations (34) and (35) it is not always possible to obtain a unique value of Δ by this procedure.

In practice ΔE_Q is not always measured at more than one temperature. Under such circumstances it is still possible to estimate the sign but no longer the magnitude of Δ from ΔE_Q. Since $q_{val.} > q_{lat.}$ we may to a first approximation consider only q_{val}. When Δ is positive the d_{xy} orbital lies lower than the d_{xz}, d_{yz} pair by definition, and from (30) it follows that q_{lat} is positive. Now for the $I = 3/2$ level of ^{57}Fe Q is a positive quantity so that when Δ is positive ΔE_Q is also positive. The converse applies when Δ is negative for a tetragonally distorted environment. When considering a trigonal distortion the combinations of one electron wave functions employed to describe the d orbitals are not the same as in the tetragonal case with the result that a negative value of Δ corresponds to a positive value of ΔE_Q and *vice-versa*. From which it follows that if we know the symmetry of the metal ions environment we can determine the sign of Δ from the sign of ΔE_Q. For the $I = 3/2$ level of ^{57}Fe ΔE_Q is positive if the $I_z = \pm 3/2$ states lie above the $I_z = \pm 1/2$ states.

With single crystal spectra, analysis of the Mössbauer line intensity as a function of orientation[36], or studying the absorption spectrum with a polarised γ-ray source[37] will yield the sign of ΔE_Q. Another method for finding the sign of ΔE_Q requires a magnetic field for the sample, this may be either an internal field for a magnetically concentrated sample[38] or a large external field (about 30 K. Oe.) for a diamagnetic or normally paramagnetic sample[39–41]. This technique has been applied to powdered samples where the two line quadrupole split spectrum is further split into a doublet and a triplet, the doublet is highest in energy when ΔE_Q is positive[42]. From E.M.R. measurements the zero field splitting parameter D, which arises from the lifting of the spin degeneracy of the ground term by spin-orbit coupling and non-cubic fields, is available. The sign of D may be found from Mössbauer studies at about 1 °K where[43] $kT < |2D|$. This forms the basis of a further way of finding the sign of ΔE_Q from the empirical relationship[44]

$$D = D_0 + f\frac{eqQ}{h} \tag{36}$$

Where D_0 represents the contribution to D from nearest neighbours in the sample and f is an experimentally determined constant.

(iii) Electron Magnetic Resonance[45]

From E.M.R. data we can obtain information relating to Δ from measurement of the anisotropic components of the g tensor. General expressions have been derived for the major components of g for systems with T_1, T_2 and E ground terms in an axial field environment[35,46–51]. In these expressions the reduction in the spin-orbit coupling constant due to covalent bonding has been neglected; to allow for this λ should be multiplied by k, the delocalisation factor, in each case.

Let us consider the $^5T_2$ ground term in a trigonal environment with Δ

positive and much greater than λ. This is a reasonable assumption since $\lambda_0 = -100\ \mathrm{cm}^{-1}$ for Fe^{II} and Δ is usually larger than this, see page 126,

then,

$$g_{\parallel} \simeq 2\left(1 - \frac{3\lambda^2}{2\Delta^2}\right)$$

and

$$g_{\perp} \simeq 2\left(1 - \frac{\lambda}{\Delta}\right) \tag{37}$$

For the $^4T_1$ ground term assuming that A is isotropic, see page 114,

$$g_{\parallel} = 2+4N(A+2)\left[\frac{3}{x^2} - \frac{4}{(x+2)^2}\right],$$

and

$$g_{\perp} = 4N\left[1 + \frac{2A}{x+2} + \frac{12}{x(x+2)}\right] \tag{38}$$

where

$$N^{-1} = 1 + \frac{6}{x^2} + \frac{8}{(x+2)^2}$$

and x is related to Δ by,

$$\Delta = -\lambda A\left(\frac{3}{x} + \frac{4}{x+2}\right) + \lambda A\frac{(x+3)}{2} \tag{39}$$

Δ is found by estimating $g_{\parallel}$, $g_{\perp}$, A and λ experimentally. If $\Delta \gg \lambda$ then equation (38) simplifies for positive values of Δ to

$$g_{\parallel} = 2$$

and

$$g_{\perp} = 2\left(1 - \frac{2\lambda A^2}{\Delta}\right) \tag{40}$$

For the $^3T_1$ ground term,

$$g_{\parallel} \simeq 2 - \frac{(A+2)\lambda^2 A^2}{\Delta^2} \tag{41}$$

and

$$g_{\perp} \simeq 2\left(1 - \frac{\lambda A^2}{\Delta}\right)$$

for the case in which $\Delta \gg \lambda$ assuming Δ is positive then,

$$g_{\parallel} = 2$$

and

$$g_{\perp} = 2\left(1 - \frac{\lambda A^2}{\Delta}\right) \tag{42}$$

For the $^2T_2$ ground term

$$g_{\|} = \frac{3(2\Delta+\lambda)}{\sqrt{(\lambda+2\Delta)^2+8\lambda^2}} - 1 \tag{43}$$

and

$$g_{\perp} = \frac{(2\Delta-3\lambda)}{\sqrt{(\lambda+2\Delta)^2+8\lambda^2}} + 1$$

for the case in which $\Delta \gg \lambda$ assuming Δ is positive then,

$$g_{\|} = 2$$

and

$$g_{\perp} = 2 - \frac{2\lambda}{\Delta} - \frac{4\lambda}{10\,q} \tag{44}$$

where the last term in the expression for $g_{\perp}$ in (44) accounts for the orbital angular momentum mixed into the ground term from the excited E term by spin orbit coupling. This term is usually very small. If there is an elongation along the z axis leading to a positive value of Δ for the ^2E ground term, then,

$$g_{\|} = 2\left(1 + \frac{4\lambda}{\Delta_1}\right)$$

and

$$g_{\perp} = 2\left(1 + \frac{\lambda}{\Delta_2}\right) \tag{45}$$

For a compression along the z axis Δ is negative and

$$g_{\|} = 2$$

and

$$g_{\perp} = 2\left(1 + \frac{3\lambda}{\Delta_3}\right) \tag{46}$$

where Δ_1 = the separation between dxy and dx^2-y^2, Δ_2 the separation between dxy and the pair dxz, dyz and Δ_3 is the separation between the $d_z{}^2$ and the d_{xz}, d_{yz} pair of orbitals.

By means of these expressions for the major components of the g tensor, expressions for the average magnetic moment due to the first order Zeeman effect may be derived[28] by using

$$g^2 = \frac{1}{3}g_{\|}{}^2 + \frac{2}{3}g_{\perp}{}^2 \tag{47}$$

and

$$P^2 = g^2\beta^2 S(S+1). \tag{48}$$

Experimentally if the sample is available as a powder or frozen solution analysis of the absorption line shape can provide values of $g_{\|}$ and $g_{\perp}$. This method[52] has been widely used for systems with $S = 1/2$. The maximum of the absorption curve corresponds to

$$h\nu = g_{\perp}\beta H$$

and the sharp cut-off gives $h\nu = g_{\|}\beta H$.

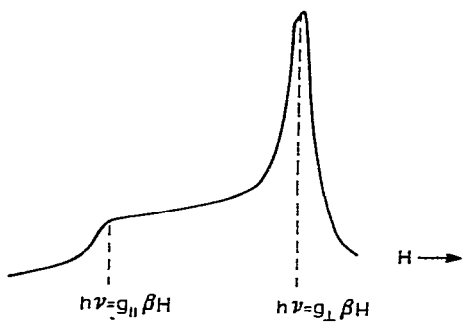

Fig. 4. E.M.R. absorption line trace for s = 1/2 assuming $g_{\|} > g_{\perp}$.

If a single crystal of the complex is available more accurate values of $g_{\|}$ and $g_{\perp}$ can be found. In the general case of an anisotropic g tensor the three principle components are referred to the x, y and z axes of the complex. If the applied field H has direction cosines l, m and n with respect to the x, y and z axes respectively, then the g value measured in the field direction is[53]

$$g = (l^2 g_x^2 + m^2 g_y^2 + n^2 g_z^2)^{\frac{1}{2}} \tag{49}$$

In the case of axial symmetry if α is the angle between the z axis and the direction of H, then (49) simplifies to

$$g = (g_{\perp}^2 \sin^2 \alpha + g_{\|}^2 \cos^2 \alpha)^{\frac{1}{2}} \tag{50}$$

The directions of the x, y and z axes may be found from the angular variation of the E.M.R. spectrum. This is studied by rotating the crystal about one of its principle axes and taking a spectrum for each orientation. In general three mountings of the crystal are necessary, although for axial symmetry two may suffice[45]. If the unit cell of the sample contains only one molecule, or a number of equivalent molecules similarly orientated, then the principle magnetic axes of the crystal coincide with the x, y and z axes of the complex molecule. In practice if all of the molecules in the unit cell are not equivalent they are often related by a simple rotation or reflection, so this presents no great extra difficulty.

(iv) Nuclear magnetic resonance[54,55]

The proton N.M.R. spectra of paramagnetic complexes can provide information about the symmetry of the metal environment by two distinct routes. An isotropic pseudocontact proton shift can arise in both solids and solutions due to the anisotropy of the g tensor of a complex with an axial distortion[56]. In a powdered solid the resonance field shift ΔH in an applied field H_0 is given by

$$\Delta H_{\text{solid}} = -(g_{\parallel}^2 - g_{\perp}^2)\frac{\beta^2 HoS(S+1)}{9KTr_i^3}(3\,\text{Cos}^2\,\theta_i - 1) \tag{50}$$

where θ_i is the angle between the principle symmetry axis of the complex and the distance vector r_i from the metal atom to the i^{th} proton. In solution the molecules tumble rapidly and the electron spin is now quantised along the axis of H_0. Under these conditions the pseudocontact shift is usually given by[57]

$$\Delta H_{\text{soln.}} = -(g_{\parallel} - g_{\perp})(g_{\parallel} + 2g_{\perp})\frac{\beta^2 HoS(S+1)}{r_i^3}\frac{(3\,\text{Cos}^2\,\theta_i - 1)}{27KT} \tag{51}$$

The ratio of ΔH_{solid} to ΔH_{soln} gives

$$\frac{3(g_{\parallel} + g_{\perp})}{(g_{\parallel} + 2g_{\perp})} \tag{52}$$

By means of (47) and (52) $g_{\parallel}$ and $g_{\perp}$ can be found provided that an average value of g is available from E.M.R. data. In practice these experiments are not always possible partly because of the line broadening that occurs on passing from solution to the solid state due to nuclear dipole–dipole coupling, and partly because the relaxation processes involved often makes the observation of N.M.R. and E.M.R. signals from the same complex mutually exclusive[58].

The second route for obtaining information about Δ is more restricted in its application and gives only its sign in favourable cases. An isotropic contact shift occurs in paramagnetic complexes due to the delocalisation of the unpaired metal *d* electrons. If the metal is symmetrically substituted the amount of delocalisation is the same on all ligands. In unsymmetrical complexes there may be a decrease in the spin densities on one ligand and a corresponding increase on the others[59]. For NiL_1L_2 complexes, where L_1 and L_2 are two different aminotroponeimines, an unsymmetrical spin density can only arise when the ^3E term lies lowest corresponding to a negative value[60] of Δ. When L_1 and L_2 are two different salicylaldimines the situation is less well defined[61].

We have seen that in principle it is possible to obtain the magnitude and sign of Δ from single crystal susceptibility and E.M.R. measurements at one temperature, from variable temperature susceptibility and Mossbauer measurements on a polycrystalline sample, from single temperature E.M.R. measurements on a powder and from the proton N.M.R. spectra of solid and solution at known temperatures.

D. RESULTS OF EXPERIMENTAL MEASUREMENTS

(i) Complexes with a $^5T_2$ ground term

The combined effect of an axial field and spin-orbit coupling considered simultaneously on the cubic field $^5T_2$ term is to produce six doublets and three singlets as shown in Fig. 5.

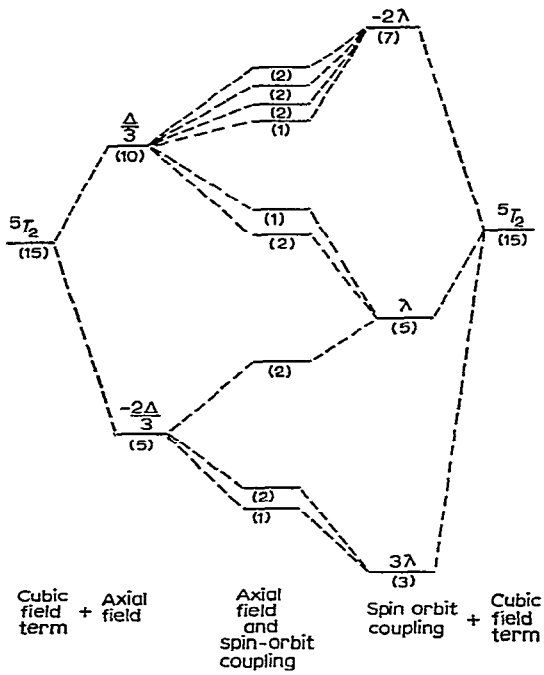

Fig. 5. Splitting pattern of a $^5T_2$ term due to an axial field and spin-orbit coupling, assuming Δ to be positive and λ negative. The degeneracy of each level is shown beneath it.

The ordering of the levels depends upon the signs and relative magnitudes of Δ and λ. The matrix for the perturbation of the fifteen ground term wavefunctions assuming no interaction with higher terms has been published[62,63]. The application of these results has led to the evaluation of Δ for a number of spin-free Fe^{II} complexes for which the free-ion value of the spin-orbit coupling constant is taken as $-103\ cm^{-1}$.

Since the expressions for the magnetic moment P, (14) (15), and the quadrupole splitting parameter ΔE_Q, (34) (35), are both dependent upon a Boltzman distribution amongst the energy levels of the system, the two may be related[64]. By taking the case of Δ being positive and summing over the resulting six doublets and three singlets we get,

$$P^2 = \frac{\sum_{n=1}^{9}\left(A_n + \frac{B_n}{y}\right)e^{a_n y}}{\sum_{n=1}^{6} 2e^{a_n y} + \sum_{n=1}^{9} e^{a_n y}} \tag{53}$$

$$\Delta E_Q = \frac{2}{7}e^2 Q(1-R)\langle r^{-3}\rangle \frac{\sum_{n=1}^{9} Cn\, e^{a_n y}}{\sum_{n=7}^{9} e^{a_n y}} \tag{54}$$

where

$$y = \frac{2S\lambda}{KT},$$

A_n, B_n, C_n and a_n are parameters which depend upon the ratio of Δ to λ. Any contribution to ΔE_Q from the lattice has been neglected in the calculation which is regretable since, as Van Vleck has pointed out for hydrated salts[12], the non-cubic field is influenced by the nature of the cation. By measuring either the average magnetic moment or ΔE at a given temperature the ratio of Δ to λ may be obtained from (53) or (54). If both P and ΔE_Q are known at the same temperature both Δ and λ are evaluated. In practice ΔE_Q is much more sensitive than P to small axial fields, also ΔE_Q is usually estimated more accurately than P so that considerable errors may be present in values of Δ and λ estimated in this manner. More accurate values of these parameters should be available by measuring either P or ΔE_Q as a function of temperature. For a spin system with a $^5T_2$ ground term we expect a Kramers singlet to lie lowest and E.M.R. results are not expected when the microsymmetry is close to cubic (Fig. 5). Weak lines have been reported for the Fe^{II} Tutton salts and $FeSiF_6\ 6H_2O$ at 20 °K but no information about Δ was obtained[35]. The estimated values of distortion and covalency parameters for a series of Fe^{II} complexes with a $^5T_2$ ground term are collected in Table 1.

The Tutton salts, $M_2^{I}SO_4FeSO_4\ 6H_2O$, are known to be tetragonal with an octahedron of water molecules elongated along the z axis[65–67], consequently a negative value for Δ is expected. The interpretation of single crystal susceptibility data of the ammonium salt agrees with this prediction[63]. These results are not in agreement with some earlier ones[68] for which a value of Δ is reported as 650 cm^{-1} at 300 °K falling to 270 cm^{-1} at 20 °K. However, it appears that these figures are in error since some of the experimental data used refers to $FeSO_4\ 7H_2O$ rather than the Tutton salt[69]. Variable temperature magnetic measurements on a polycrystalline sample of the Tutton salt[62] have been analysed in favour of a positive value for Δ, agreeing with susceptibility and specific heat data at liquid helium[70,71], and liquid hydrogen[72] temperatures. These latter results have been interpreted on the basis of a tetragonal field component[28] of between 100 and 1000 cm^{-1}. Quadrupole splitting data suggests that the sign of Δ is positive[42] and that it is equal to 280 cm^{-1}

TABLE 1

FITTING PARAMETERS OBTAINED FOR SOME HIGH-SPIN IRON(II) COMPLEXES

Complex	Δ (cm^{-1})	λ (cm^{-1})	k	*Ref.*
$(NH_4)_2SO_4FeSO_46H_2O$	−1070	−100	0,8	63*
	650	−100		68*
	410	−90	1,0	62
	280	−80		22, 34*
$K_2SO_4FeSO_46H_2O$	−500	−100	0,8	63*
$FeSiF_66H_2O$	760	−80	0,7	63*
	730	−100		74
	1200	−100		75
	750	−100	0,7	62
	760	−80		22
$FeSO_47H_2O$	410	−90	0,85	62
	890	−80		22
$FeSO_4$	1020	−80		22
$FeCl_24H_2O$	140	−70	0,6	83
	1830	−80		22
$FeCl_2$ $2H_2O$	520	−100	1,0	88
Fe Oxalate $2H_2O$	530	−80	0,6	22, 42, 89
	200	−70	0,6	83
FeF_2	1600	−67		22
$FeCl_2$	120	−95		93
Fe(lactate)$_2$ $5/2H_2O$	60	−60	0,5	83
$Fe(en)SO_4$ $4H_2OH_2SO_4$	310	−90	0,65	62
Fe(αpicolinic acid-*N*-oxide)$_2$ $2H_2O$	120	−63	0,9	62
Fe(pyrazine αα′dicarboxylate) $2H_2O$	280	−77	0,8	62
Fe(pyrazine αcarboxylate)$_2$ $2H_2O$	160	−80	0,7	62
$Fe(pyrazine)_2(NCS)_2$	−210	−70	0,7	62
	0	−80	0,7	
$Fepy_4(NCS)_2$	140	−65	1,0	62
	480	−80	0,7	64
	280	−70	0,7	83
$Fepy_4Cl_2$	540	−82		38
	2000	−80		64
$Fepy_4Br_2$	1500	−80		64
$Fepy_4I_2$	400	−80		64
$Fepy_4I_2$ 2py	450	−80		64
$Fepy_4(OCN)_2$	1500	−80		64
$Fepy_4(OCN)_2$ 2py	1700	−80		64
Feγ-pic_4Cl_2	520	−82		20
Feγ-pic_4Br_2	200	−82		20
Feγ-pic_4I_2	40	−82		20
Feγ-$pic_4(NCS)_2$	±500	−82		20
$Fephen_2Cl_2$	1900	−65		64
	720			91
	880	−80	0,8	90
$Fephen_2Br_2$	720	−80	0,8	90
	640			91
$Fephen_2(N_3)_2$	−4000	−80	0,8	90
	880	−80	0,8	
	650			91
$Fephen_2(OCN)_2$	1440	−80	0,8	90
	660	−80	0,8	91

TABLE 1 *(Continued)*

Complex	Δ (cm^{-1})	λ (cm^{-1})	k	*Ref.*
$Fephen_2(HCOO)_2$	{ −2000	−80	0,8 }	90
	{ 560	−80	0,8 }	
	490			91
$Fedipy_2(SCN)_2$	{ 400	−80 }		92
	{ 500	−100 }		
$Fedipy_2Cl_2$	600			91
$Fephen_2(CH_3COO)_2$	580			91
$FeIQ_4Cl_2$	600	−82		20
$FeIQ_4Br_2$	360	−82		20
$FeIQ_4I_2$	80	−82		20
$FeIQ_4(NCS)_2$	±370	−82		20
Fe[poly(1-pyrazolyl)borate]$_2$	1000	−80	0,9	81

{ } Indicates that more than one set of the fitting parameters may be used to accommodate the experimental data.
* Indicates that some of the parameters are found to vary with temperature in which case the room temperature values are quoted.

for an axial field and an additional 80 cm^{-1} if a rhombic field is considered[22,34] The temperature dependence of Δ is thought to be due to an isotropic thermal expansion.

The experimental results for the principle suspectibilities[72] of the potassium Tutton salt have been analysed for the temperature range between 185.6 °K and room temperature in terms of $\Delta = -500$ cm^{-1} and k increasing from 0.6 to 0.8 over this temperature range[63]. These values are unreconcilable with the susceptibility data at 86.3 °K, which probably indicates an inaccuracy in the experimental data. This should be checked, if possible, by different physical measurement in order to obtain the best set of parameter values.

Recently the experimental values of the principle magnetic moments of $FeSiF_6 6H_2O$ have been accounted for on the basis of the value of Δ varying from 760 cm^{-1} at 77.3 °K to 600 cm^{-1} at liquid helium temperatures[63]. This is in satisfactory agreement with earlier susceptibility data[74–76] and recent polycrystalline susceptibility measurements[62], which have predicted values of Δ between 730 and 1200 cm^{-1}. Quadrupole splitting data[22,37,42] also suggest an axial field[22] of 760 cm^{-1}. The substantial agreement on the axial component of the crystalline field in this molecule should be compared with neutron defraction studies which indicate that the iron atom is surrounded by an octahedron of water molecules elongated along the three-fold axis[77]. The small value of k reported for $FeSiF_6$-$6H_2O$ and the Tutton salts is unexpected, since it implies an appreciable degree of electron delocalisation. This is thought to occur by π bonding to the water molecules, which is usually only of minor importance for water.

Single crystal susceptibility measurements have been reported[78] for $FeSO_4$-$7H_2O$. Since the unit cell contains 8 molecules whose mutual orientation is unknown[79] the data cannot be unambiguously analysed. In the octahedron of water

molecules surrounding the iron atom, one of the Fe-OH_2 distances is longer than the rest[80], consistent with the axial field implied by the analysis of powder susceptibility measurements[62]. The nuclear quadrupole splitting parameter suggests an axial field of 890 cm^{-1}, and a further rhombic[22] field component of 410 cm^{-1}. Other Mössbauer data agree with a positive sign of Δ for this molecule[42,81].

The variable temperature susceptibility data for $FeSO_4$ appears not to have been analysed[82]. However, the Mössbauer data suggest an axial field splitting of 1020 cm^{-1} and a rhombic field component[22,38,42] of 660 cm^{-1}.

The variable temperature powder susceptibility measurements on $FeCl_2$-$4H_2O$ have been analysed in favour of a positive value of Δ[83] which is reconcileable with the known structure[84] (Fig. 6).

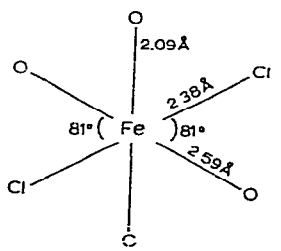

Fig. 6. Structure of $FeCl_24H_2O$. Apart from the two angles of 81° the others are all approximately 90°.

It is anticipated that the two short Fe–O distances could produce an axial field component leaving an orbital singlet as the ground term. Mössbauer and electronic spectral data have also been interpreted in favour of a positive value for $\Delta = 1830$ cm^{-1} with an additional rhombic field component[22,36,42,85] of about 1080 cm^{-1}. The quadrupole splitting of the corresponding bromide is also indicative of a positive[20,85] value of Δ.

$FeCl_22H_2O$ is polymeric with bridging chloride ions, each iron atom has a tetragonal environment with four chloride ions in a plane and two *trans* water molecules[86]. The corresponding bromide is isomorphous[87]. Single temperature Mössbauer data has been interpreted in favour of a positive value of Δ for both of these molecules[85,88].

Structural data appear not to be available for most of the other complexes listed in Table 1. For the majority of these complexes Δ is small and shows no obvious relationship to the ligands present in the complex. In particular the reduction in Δ from 1600 to 120 cm^{-1} in passing from FeF_2 to $FeCl_2$ is rather surprising, but due to antiferromagnetic behaviour the Mössbauer data is unlikely to be challenged by a magnetic investigation. The uncertainty in interpreting the powder susceptibility data is clearly shown by the different sets of parameter values quoted[62] for $Fe(pyrazine)_2(NCS)_2$. This uncertainty largely arises from the small value of λ for the ferrous spin-free ion which produces only a small variation in the magnetic

moment between room and liquid nitrogen temperatures. Because of this an error of up to $\pm 25\%$ in Δ is possible and a completely independent fit for the parameters Δ, λ and k is not generally possible from powder susceptibility results. Data at liquid helium temperatures would help to produce a more reliable set of parameters. An uncertainty in the sign of Δ appears to exist for the substituted thiocyanate complexes reported in Table 1, this could be an indication that they are polymeric and that the theory for axial symmetry is no longer applicable to them. The parameters for the $Fepy_4X_2$ complexes have been estimated from single temperature susceptibility and Mössbauer data[64]. A 20% reduction in λ has been assumed in comparison with data on similar complexes. Many of the values of Δ estimated in this way for these complexes are considerably larger than for analogous pic, phen, dipy or IQ complexes. This may be largely due to differences in experimental data as noted by König *et al.*[90] for (Fe $phen_2Cl_2$).

One of the polymorphs of (Fe $dipy_2$ $(NCS)_2$) is of sufficiently low symmetry to provide E.M.R. data which have been interpreted in favour of an axial field splitting of between 400 and 500 cm^{-1} when λ is allowed to vary[92] between -80 and $-100\ cm^{-1}$. This is in good agreement with values derived by other techniques on related complexes. The amount of electron delocalisation for the complexes in Table 1 varies between 0 and 50% but there appears to be no obvious correlation with the π bonding character of the ligands involved.

There does not appear to be any experimental data interpreted in terms of an axial field distortion for the $^5T_2$ ground term arising from metals with a d^4 configuration in tetrahedral complexes.

(ii) Complexes with a $^4T_1$ ground term

The six doublets that arise from the $^4T_1$ term when an axial field and spin orbit coupling are considered simultaneously are shown in Fig. 7. The interaction matrix for the 12 ground term wave functions, including the perturbation produced by the excited ^4P term, has been reported[49]. The equations expressing the magnetic susceptibility as a function of Δ, λ and temperature have also been discussed[94,161]. These have been used to evaluate Δ, λ and k from susceptibility and E.M.R. data for some spin-free Co^{II} complexes in distorted octahedral environments, for which the free ion value of λ is taken as $-180\ cm^{-1}$, as reported in Table 2.

Van Vleck[12] has shown from simple one-electron arguments that, by assuming identical ligand environments in both cases, the axial fleld splitting in octahedral spin-free Fe^{II} and Co^{II} complexes should be of opposite sign. This appears to be in harmony with the data on the Fe^{II} and Co^{II} complexes of the types $MSiF_6$ $6H_2O$ and M(poly(1-pyrazolyl)borate)$_2$, for which the iron complexes have positive values of Δ and the cobalt complexes negative values, (Tables 1 and 2). For the ammonium Tutton salts there appears to be some ambiguity in the sign

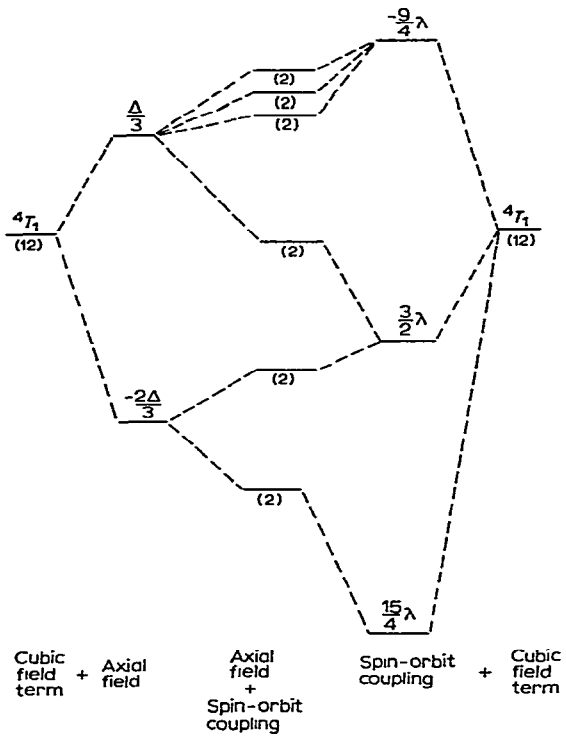

Fig. 7. Splitting pattern of a $^4T_1$ term due to an axial field and spin-orbit coupling, assuming Δ to be positive and λ negative.

of Δ for both the iron and the cobalt complexes. Since the structure consists of an elongated octahedron of water molecules surrounding the metal atom[65–67] simple arguments would be in favor of a negative value of Δ for the iron salt and a positive one for the cobalt salt. However negative values of Δ are most commonly reported for the cobalt salt[58,94,96–98] and positive ones for the iron salt (Table 1). Negative values of Δ are reported for both of the potassium Tutton salts which is quite unexpected. For the pairs of complexes $MSO_4\,7H_2O$, $Mpy_4(NCS)_2$ and $Mpy_4(NCO)_2$ the positive Δ value reported for the iron complex suggests that the cobalt value should be negative in each case. Unfortunately the powder susceptibility data from the cobalt complexes, collected between room temperature and 78 °K, cannot be interpreted unambiguously in favour of a particular value[83] of Δ. However recent measurements at liquid helium temperatures are more encouraging and should be more widely employed[101].

The crystal structures of $Co(acac)_2\,2H_2O$[102] and $Co(CH_3COO)_2\,4H_2O$[103] indicate a tetragonally elongated octahedron of oxygen atoms surrounding the cobalt atom, hence the positive values of Δ reported in Table 2 are favoured for these complexes.

There appears to be no independent information available concerning the

molecular structures of the remaining complexes reported in Table 2. Because it is generally possible to fit the powder susceptibility results, at temperatures above that of liquid nitrogen, to more than one set of parameters little can be profitably said about the effects of non-cubic fields in these complexes until more data is available.

No experimental data, which could be interpreted in terms of an axial field splitting, appear to have been reported for tetrahedral complexes with the d^3 configuration and a $^4T_1$ ground term.

TABLE 2

FITTING PARAMETERS OBTAINED FOR SOME HIGH-SPIN COBALT(II) COMPLEXES

Complex	Δ (cm^{-1})	λ (cm^{-1})	k	*Ref.*
$(NH_4)_2SO_4CoSO_4\ 6H_2O$	330	−145	0,9	98
	−775	−180	1,0	
	−1090	−180	1,0	96
	−700	−180		97
	−1000	−180	1,0	94*
	−1000	−180	1,0	49
$K_2SO_4CoSO_4\ 6H_2O$	−250	−180	1,0	94
$(NH_4)_2BeF_4Co(BeF_4)\ 6H_2O$	−850	−180	1,0	94
$CoSiF_6\ 6H_2O$	−500	−180	1,0	49
$CoSO_4\ 7H_2O$	350	−130	0,8	83
	−1300	−160	0,9	
$CoCl_2\ 6H_2O$	375	−150	0,8	98
	−1030	−180	0,9	
	200	−180	1,0	100
$Co(CH_3COO)_2\ 4H_2O$	450	−160	0,9	83
	−650	−160	1,0	
$KCo(acac)_3$	420	−145	0,8	83
	−950	−160	0,95	
$Co(acac)_2\ 2H_2O$	350	−160	0,9	83
	−1200	−170	0,95	
$Cophen_3(ClO_4)_2$	230	−110	0,6	83
	−980	−145	0,7	
$Codipy_3(ClO_4)_2$	370	−125	0,7	83
	−320	−125	0,8	
$Co(opd)_6Cl_2$	350	−145	0,8	83
	−1400	−180	0,9	
$Co[(C_6H_5)_2CH_3AsO]_4(ClO_4)_2\ H_2O$	550	−145	1,0	95
$Co[(C_6H_5)_2CH_3AsO]_4(NO_3)_2\ H_2O$	550	−160	0,9	95
$Copy_4(ClO_4)_2$	350	−145	0,9	83
	−700	−145	1,0	
$Copy_4(NCS)_2$	350	−160	0,9	83
	−400	−160	0,9	
$Copy_4(NCO)_2$	380	−145	0,9	83
	−900	−170	0,95	
$Copy_2Br_2\ 2H_2O$	370	−142	0,8	83
	−950	−160	0,9	
$Copy_2Cl_2\ 2H_2O$	430	−180	1,0	98
	−774	−180	1,0	
Co[hydrotris(1-pyrazolyl)borate]$_2$	−1900	−145	0,9	99
Co[tris(1-pyrazolyl)methane]$_2(NO_3)_2$	−2136	−145	0,9	99

Footnotes see Table 1.

(iii) Complexes with a $^3T_1$ ground term

A $^3T_1$ ground term is found for complexes with the following configurations and symmetries, d^8 tetrahedral, d^4 spin-paired octahedral and d^2 spin-free octahedral. The perturbations produced by an axial field component and spin-orbit coupling considered together produce three doublets and three singlets. In the absence of a magnetic field a Kramers singlet lies lowest so that under normal circumstances an E.M.R. signal is not expected for these complexes.

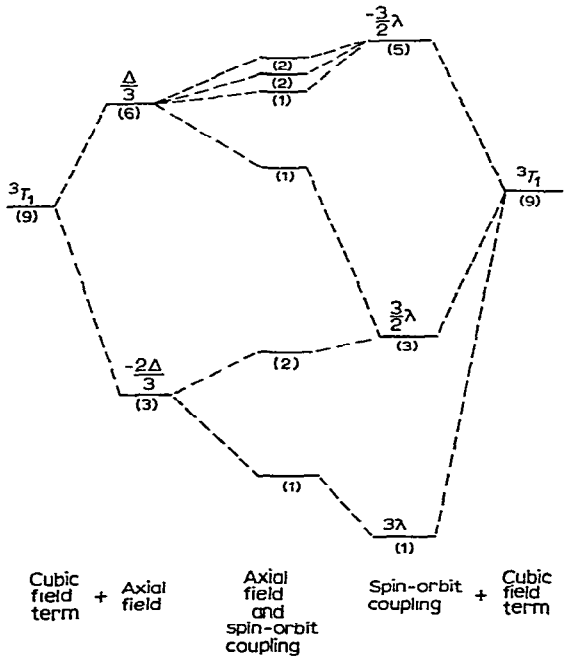

Fig. 8. Splitting pattern of a $^3T_1$ term due to an axial field and spin-orbit coupling, assuming Δ to be positive and λ negative.

The interaction matrix for the $^3T_1$ term including the effects of spin-orbit coupling, either a tetragonal or trigonal field component and coupling with the excited ^3P term has been applied to the temperature variation of the magnetic moment of a series of tetrahedral Ni^{II} complexes[104], spin-paired Cr^{II}, Mn^{III} and Fe^{IV} complexes[113,116] and spin-free V^{III} complexes[120,124]. The parameters for the Ni^{II} complexes listed in Table 3 were obtained by assuming that the free-ion value of the spin-orbit coupling constant $\lambda_0 = -315\ cm^{-1}$.

Single crystal X-ray studies have been reported for some of these Ni^{II} complexes. In the triphenymethylarsonium salt of the tetrachloronickelate ion the Ni^{II} ion has a regular tetrahedral environment to within experimental error[108], whereas in the corresponding tetraethylammonium salt it has a D_{2d} environment with pairs

TABLE 3

FITTING PARAMETERS OBTAINED FOR SOME TETRAHEDRAL NICKEL(II) COMPLEXES

Complex	Δ (cm^{-1})	λ (cm^{-1})	k	*Ref.*
$[(C_2H_5)_4N]_2NiCl_4$	718	−194	1,0	104
$[(C_6H_5)_3CH_3As_2]_2NiCl_4$	718	−194	1,0	104
Cs_3NiCl_5	600	−150	0,95	104
$[(C_6H_5)_3AsO]_2NiCl_2$	700	−140	1,0	104
$[(C_6H_5)_3P]_2NiCl_2$	845	−130	0,55	104
$[(C_2H_5)_4N]_2NiBr_4$	650	−130	1,0	104
	1020	−315	1,0	105*
$[(C_6H_5)_3CH_3As]_2NiBr_4$	650	−130	1,0	104
$[(C_2H_5)_4N][(C_6H_5)_3PNiBr_3]$	750	−150	0,85	104
	1050	−310	0,9	106
	2100	−310	0,9	
$[(C_2H_5)_4N][Benzimidazole\ NiBr_3]$	660	−220	0,7	107
$[(C_6H_5)_3P]_2NiBr_2$	845	−130	0,55	104
$[(C_6H_5)_3PO]_2NiBr_2$	585	−130	1,0	104
$[(C_6H_5)_3AsO]_2NiBr_2$	610	−130	1,0	104
$[(C_6H_5)_3CH_3As]_2NiI_4$	900	−150	0,8	104
$[(C_6H_5)_3P]_2NiI_2$	1830	−208	0,7	104
	910	−140	0,55	
$[(C_6H_5)_3PO]_2NiI_2$	975	−195	1,0	104
$Nipy_2I_2$	1260	−180	0,8	104
	840	−140	0,7	
$Ni\beta\text{-}pic_2I_2$	1688	−225	0,8	104
	1120	−140	0,7	
$[(C_6H_5)_3PO]_2Ni(NO_3)_2$	1120	−140	0,85	104

Footnotes see Table 1.

of Cl–Ni–Cl angles equal[109] to 106,83° and 110,81°. Because of their structural difference it is surprising that identical values of Δ have been reported for these two complexes. Cs_3NiCl_5 which has a lower value of $\Delta = 600\ cm^{-1}$, is isomorphous with the corresponding cobalt salt which has Cl–Co–Cl angles of 106° and 111° taken in pairs[110]. If it is assumed that the Co and Ni salts are strictly isostructural then the axial field parameter for Cs_3NiCl_5 is expected to be very similar to that for $[(C_2H_5)_4N]_2NiCl_4$ and different from that for $[(C_6H_5)_3CH_3As]_2NiCl_4$. The reported values of Δ are most probably an indication of the reliability of data obtained from polycrystalline susceptibility measurements. Lohr and Lipscomb[111] have shown by molecular orbital calculations on the $NiCl_4^{2-}$ ion that an elongation leading to a structure with D_{2d} symmetry and angles of about 118° and 104° is necessary to obtain a stabilisation energy of about 1000 cm^{-1}. This appears to be in reasonably close agreement with the values of Δ reported in Table 3 for the $NiCl_4^{2-}$ ions in $[(C_2H_5)_4N]_2NiCl_4$ and Cs_3NiCl_5.

Single crystal X-ray data indicates that $[(C_6H_5)_3P]_2NiCl_2$ is a flattened tetrahedron with the angles Cl–Ni–Cl = 123° and P–Ni–P = 117°[112]. The reported value of Δ for this complex is 845 cm^{-1} comparable to the values listed for the more symmetrical complexes; this probably means that Δ is surprisingly

insensitive to changes in the structural environment of the Ni^{II} ion. From the data reported in Table 3 for the less symmetrical complexes it appears that the decrease in symmetry is more accurately reflected by a decrease in the electron delocalisation parameter k than by a significant change in Δ. The most striking reduction in k occurs when the halogens are replaced by triphenylphosphine. The experimental data for the NiL_2I_2 complexes, with L = Py, β-pic or $(C_6H_5)_3P$ may be fitted by either of two combinations of parameters. For these complexes it does seem that a change in either k or Δ can be used to account for the magnetic results.

In a cubic field the orbital degeneracy of the $^3T_1$ term is raised by spin orbit coupling alone to the extent of 3/2 λ which is probably about 250 cm^{-1} for the Ni^{II} complexes. This should be sufficient to satisfy the requirements of the Jahn–Teller theorem at room temperature and below, so that it seems inappropriate to invoke effects arising from this theorem to account for the relative constantcy of Δ. Recent measurements of susceptibilities at liquid helium temperatures suggest that more reliable estimates of the fitting parameters are available in this temperature range[107]. More work of this type is expected in the future.

The fitting parameters arising from the interpretation of powder susceptibility measurements for some spin-paired d^4 octahedral complexes are reported in Table 4. It is assumed that the free-ion values of the spin-orbit coupling constant λ_0 are 115 cm^{-1} for Cr^{II}, 180 cm^{-1} for Mn^{III} and 260 cm^{-1} for Fe^{IV}.

Although different authors report comparable magnitudes for the axial field splitting in the Cr^{II} complexes there appears to be ambiguity in estimating the sign of Δ. Due to the small value of the spin-orbit coupling constant for Cr^{II} the magnetic moment does not vary appreciably with temperature so that the magnetic

TABLE 4

FITTING PARAMETERS OBTAINED FOR SOME SPIN-PAIRED d^4 COMPLEXES

Complex	Δ (cm^{-1})	λ (cm^{-1})	k	*Ref.*
$Crdipy_3Cl_2$	>2000	100		113
	−900	90	0,5	116
$Crphen_3Cl_2\ 2H_2O$	>2000	100		113
$Crdipy_3Br_2$	600	100		113
	−600	90	0,8	116
$Crdipy_3Br_2\ 4H_2O$	700	100		113
	640	90	0,6	115
$Crphen_3Br_2\ 2H_2O$	1000	100		113
	−1000	100	0,95	116
$Crdipy_3I_2$	−600	100		113
	−350	100	0,95	116
$Crphen_3I_2\ 2H_2O$	>2000	100		113
$K_3Mn(CN)_6$	100	150		113
	190	140		114
$[Fe(diars)_2Br_2]\ [BF_4]_2$	1400	230		113
$[Fe(diars)_2Cl_2]\ [BF_4]_2$	>4650	230		113

data is open to more than one possible interpretation. In the absence of reliable structural information it is not possible to conclude whether the complexes consist of compressed or elongated octahedral structures. The apparent dependence of Δ on the degree of hydration and the differences in the value of Δ between the corresponding tris phen and tris dipy complexes is unexpected when compared with data on some comparable Fe^{III} complexes, (see Table 6).

The general agreement on a small axial field splitting for $K_3Mn(CN)_6$ indicates the expected presence of a highly symmetrical environment and is in satisfactory agreement with data on the corresponding Fe^{III} complex, (see Table 6).

The very large difference in the distortion of the two Fe^{IV} complexes reported in Table 4 is not readily explained since the replacement of bromide by chloride is not expected to appreciably increase the axial field component in the complex.

In Table 5 the fitting parameters for some V^{III} complexes are reported. λ_0 is taken to be 105 cm^{-1}.

The alums are known to be trigonally distorted from X-ray evidence and a positive value of Δ is predicted for the alum salts of V^{III}. All of the reported data

TABLE 5

FITTING PARAMETERS OBTAINED FOR SOME VANADIUM(III) COMPLEXES

Complex	Δ (cm^{-1})	λ (cm^{-1})	k	*Ref.*
$(NH_4)_2SO_4VSO_4$ $12H_2O$	1390	64		118
	670	70		119
	2000	105	0,8	28
	540	60	0,8	124*
†$(NH_2)_3CV(SO_4)_2$ $6H_2O$	880	80	0,6	117
	770	70	0,6	
$[(urea)_6V]Br_3$	800	75	0,6	117
$[(urea)_6V]$ $(ClO_4)_3$	840	105	0,4	120
$K_3[V(SCN)_6]4H_2O$	190	95	0,5	120
VCl_3 $6H_2O$	750	75	0,8	117
	650	65	0,6	
$(NH_4)_3VF_6$	160	80	0,4	120
$K_2(VF_5H_2O)$	540	90	0,75	120
$Cs(VF_42H_2O)$	712	75	0,4	120
VCl_3 3THF	665	95	0,9	120
VCl_3 $3(CH_3CN)$	880	80	0,9	120
VCl_3 $3(C_2H_5CN)$	480	80	0,4	120
$K_3[V(malonate)_3]$	1100	100	0,9	120
	250	50	0,4	
$K_3[V(oxalate)_3]$ $3H_2O$	700	50	0,4	120
	930	60	0,75	124*
$Cs_3[V(oxalate)_3]$ $3H_2O$	600	50	0,5	120
$V(oxyquinoline)_3$	700	70	0,4	120
$V(benzoylacetone)_3$	790	75	0,6	120

Footnotes see Table 1.
† Guanidinium salt.

for $(NH_4)_2V(SO_4)_212H_2O$ in Table 5 are in agreement with this prediction although the magnitude of the axial field splitting is not finalised and may even be temperature dependent[124]. In vanadium doped corundum Δ has been variously reported[121,122] as about 1200 cm^{-1} or approximately[123] 960 cm^{-1}, which indicates that the splitting of about 1300 to 1400 cm^{-1} obtained by single crystal anisotropy measurements on the alum[118,124] is very reasonable. The magnetic moment of the alum in solution is the same as in the solid state[28] which indicates that Δ does not arise from packing effects in this case but may be the result of the Jahn–Teller effect operating due to the small splitting produced by spin-orbit coupling in V^{III}.

Polarised crystal spectra of guanidine aluminium sulphate hexahydrate doped with V^{III} indicate that the axial field splitting of the vanadium ground term[125] is approximately 1000 cm^{-1}. This is in reasonable agreement with the two possible values of Δ for $C(NH_2)_3V(SO_4)_26H_2O$ derived from average magnetic susceptibility measurements[117].

The low values of Δ reported for $(NH_4)_3VF_6$ and $K_3(V(SCN)_6)$ are indicative of a fairly symmetrical environment, but the much larger axial field splitting implied for the two hexa–urea complexes and $VCl_3 \cdot 6H_2O$ is unexpected. Some independent structural data on these complexes would be very enlightening. A substantial increase in Δ occurs when a water molecule is substituted into the VF_6^{3-} ion, and a further smaller increase occurs when a second water molecule is substituted. This possibly reflects upon a *trans* substitution for the second water molecule since this would produce a higher symmetry than *cis* substitution.

The differences in the axial field splitting of the VCl_3Y_3 adducts are probably greater than the experimental error in analysing powder susceptibility data and as such are not easily explained. The tris chelate complexes included in Table 5 have fairly large values of Δ which are indicative of a trigonal distortion common to complexes of this type.

As with other series of complexes those with $^3T_1$ ground terms have Δ values which do not appear to be closely related to the symmetry of the complex, nor do changes in k always follow relative changes in the π bonding capacity of the ligands.

(iv) Complexes with a $^2T_2$ ground term

Until now we have only considered the cases of axial field splitting for which Δ and λ are of the same order of magnitude. This has restricted the examples to complexes containing metals from the first transition series. In the later series spin-orbit coupling usually represents the major perturbation and it then becomes necessary to consider other energy level compilations[126]. The exception to this argument occurs with the $^2T_2$ ground term where the splitting is qualitatively the same under both Russell–Saunders and j-j coupling and depends only upon the

relative signs[127] of Δ and λ. Consequently some complexes of the second and third row transition metals are included in this section.

A^2T_2 ground term is present in complexes with the following configurations and symmetries, d^5 spin-paired octahedral, d^1 octahedral and d^9 tetrahedral. Expressions comparable to equations (53) and (54), relating the magnetic moment and quadrupole splitting parameter in terms of their mutual dependence upon a Boltzman distribution function, have been developed for spin-paired Fe^{III} complexes with a $^2T_2$ ground term[128,129]. The elements of the interaction matrix and the interpretation of both static and resonance magnetic studies have been widely discussed for complexes with a $^2T_2$ ground term[114,130–138]. The splitting of this term by Δ and λ into three doublets is shown in Fig. 9.

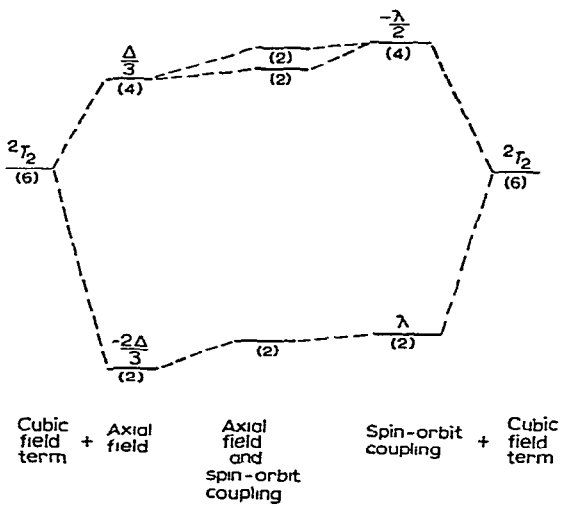

Fig. 9. Splitting pattern of a $^2T_2$ term due to an axial field and spin-orbit coupling, assuming Δ to be positive and λ negative.

The parameters obtained by fitting experimental data for complexes of Mn^{II} Fe^{III}, Ru^{III} and Os^{III} assuming the free-ion spin-orbit coupling constants to be $-300\,cm^{-1}$, $-440\,cm^{-1}$, $-1180\,cm^{-1}$ and $-3500\,cm^{-1}$ respectively are reported in Table 6.

The range of values reported for the axial field splitting of the $Fe(CN)_6^{3-}$ ion from single crystal and powder susceptibility measurements as well as Mössbauer and E.S.R. data gives an indication of the reliability that may be placed upon reported values of Δ. The smaller values of Δ, indicating a symmetric environment for the Fe atom, seem most reasonable both intuitively and by comparison with the data on the corresponding Mn^{III} complex, (see page 124). The apparent dependence of Δ upon the degree of hydration requires explanation.

The larger values of Δ and of k reported for the tris phen and dipy complexes

TABLE 6

FITTING PARAMETERS OBTAINED FOR SOME SPIN-PAIRED d^5 COMPLEXES

Complex	Δ (cm^{-1})	λ (cm^{-1})	k	*Ref.*
$K_3Fe(CN)_6$	230	−350	0,85	128
	0	−400	0,8	131
	115	−278	0,87	136
	±200	−400	0,9	134, 139
$Na_3Fe(CN)_6H_2O$	460	−350	0,85	128
$Cu_3[Fe(CN)_6]_2\ 4H_2O$	690	−350	0,85	128
$Fephen_3(ClO_4)_2\ 3H_2O$	600	−400	1,0	131
$Fedipy_3(ClO_4)_2\ 3H_2O$	600	−300	1,0	131
$[Fephen_2(CN)_2]\ (ClO_4)$	393	−437	0,95	138
$[Fephen_2(CN)_2]NO_3\ 4H_2O$	644	−460	1,0	138
$[Fedipy_2(CN)_2]\ (ClO_4)$	414	−414	0,9	138
$[Fedipy_2(CN)_2]NO_3$	538	−414	0,9	138
Fe(N-methyl-N-phenyl DTC)$_3$	110	−250	0,79	140
Fe(N-ethyl-N-phenyl DTC)$_3$	66	−200	0,71	140
Fe(N-isoamyl-N-phenyl DTC)$_3$	57	−150	0,61	140
Fe(NN-dicyclohexyl DTC)$_3$	126	−400	1,0	140
Fe(NN-di-isopropyl DTC)$_3$	230	−350	0,87	128
$K_4Mn(CN)_6\ 3H_2O$	400	−200	0,75	131
	150	−240	0,85	134
	170	−240	0,90	
	500		0,74	136
	760	−252	0,9	139
$[Ru(NH_3)_6]Cl_3$	0	−1000	1,0	138
	0	−1000	1,0	139
	−1000	−1000	0,95	
$[Ru(NH_3)_6]\ (NO_3)_3\ 3H_2O$	500	−1000	1,0	138
	−1000	−1000	1,0	
	±1000	−1000	0,95	139
$[Ru(NH_3)_5Cl]Cl_2H_2O$	0	−600	0,9	138
	>2000	−1000	0,95	139
$Ru(acac)_3$	−5000	−1000	0,7	138
	>2000	−1000	0,95	139
$[Rudipy_2Cl_2]Cl\ 2H_2O$	−8800	−1100	0,85	141
	1200	−600	0,75	
$[Rudipy_2Cl_2]ClO_4$	−8800	−1100	0,8	141
	2000	−600	0,7	
[dipyH] $[Rudipy\ Cl_4]H_2O$	0	−550	0,9	138
	>3000	−1000	0,95	139
$Rupy_3Cl_3$	−3300	−1000	0,7	141
	900	−900	0,7	
Ruβ-pic_3Cl_3	−4400	−1150	0,75	141
	1100	−1100	0,7	
Ruγ-pic_3Cl_3	−11500	−1150	0,7	141
	1725	−600	0,55	
$[Osphen_2Cl_2]ClO_4$	−31200	−1600	0,6	141
	2400	−3000	0,85	
$Ospy_3Cl_3$	−24800	−1600	0,6	141
	2200	−2800	0,85	
Osγ-pic_3Cl_3	−31200	−3000	0,85	141
	−3400	−1600	0,75	

Footnotes see Table 1.

of Fe^{III} in comparison with the tris dithiocarbamate derivatives are unexpected. It is also surprising that Δ appears to decrease when either phen or dipy is replaced by two cyanide ions.

The small variation of the average magnetic moment with temperature gives rise to the extensive ranges of fitting parameters that are reported for the Ru^{III} and Os^{III} complexes[138,139,141]. This emphasises the possible ambiguities that may arise in interpreting powder susceptibility data. The situation is particularly disturbing for the osmium complexes where both the sign and magnitude of Δ are undetermined. In general the axial field splitting appears to be larger for the Ru^{III} and Os^{III} complexes than is found in most first row complexes. In the absence of reliable structural data or more accurate experimental data such as might be expected from single crystal susceptibility or E.M.R. measurements the situation cannot be claried further.

The fitting parameters for some complexes with the d^1 configuration are reported in Table 7. The free-ion values of the spin-orbit coupling constants are taken to be 154 cm^{-1}, 250 cm^{-1}, 1030 cm^{-1} and 2500 cm^{-1} for Ti^{III}, V^{IV}, Mo^{V} and W^{V} respectively.

The data for the alum $Cs_2(SO_4)12H_2O$ have been derived from a number of experimental sources; this is reflected in the variation of the reported values of the axial field splitting parameter. It is noteworthy that in all cases Δ is positive for the titanium alum and the same applies to the alum of V^{III} reported in Table 5. From Van Vlecks' one electron arguments[12] it is expected that Δ would be of opposite sign for these two alums. No ready explanation is available to account for the experimentally determined values of Δ.

The axial field splitting reported for the two complexes containing the $[Ti(urea)_6]^{3+}$ ion is of the same sign as that reported in Table 5 for two similar V^{III} complexes. Although Δ is about 50% smaller in the Ti^{III} complexes it is still rather high for the anticipated cubic symmetry of the metal atom. The distortions reported for the other Ti^{III} complexes in Table 7 do not appear to bear any obvious relationship to the nature of the ligands in the complex. Differences in the values of Δ are as likely to be due to the errors involved in obtaining the experimental data and interpreting it as to any chemically meaningful changes. It is to be hoped that structural studies, E.M.R. measurements or susceptibility data at liquid helium temperatures will become available to help in the interpretation of the axial field splitting in these complexes.

The experimental data reported in Table 7 for the V^{IV} complexes were again derived from average susceptibility measurements[146]. Since the average magnetic moment is not very temperature dependent a range of values for the curve fitting parameters is available for most of the complexes studied. It is gratifying to observe that the complexes containing the vanadyl ion, VO^{2+}, experience a larger axial field splitting than those containing the hexachloro vanadium^{IV} ion.

The results of curve fitting for the Mo^{V} and W^{V} complexes included in Table

TABLE 7

FITTING PARAMETERS OBTAINED FOR SOME d^1 COMPLEXES

Complex	Δ (cm^{-1})	λ (cm^{-1})	k	*Ref.*
$Cs_2SO_4Ti(SO_4)_2$ $12H_2O$	200	154	0,9	134
	750	152	0,95	139
	800	150	0,65	143
	350	93	0,7	144
	500	154	0,87	148*
	140	140	0,6	45
$[(urea)_6Ti](ClO_4)_3$	400	120	0,8	142
$[(urea)_6Ti]I_3$	480	160	0,65	145
$[(C_2H_5)_4N][TiCl_4 2CH_3CN]$	600	150	0,55	145
$TiCl_3 3CH_3CN$	600	155	0,8	139
	500	120	0,8	
	600	150	0,6	142
$TiCl_3 3THF$	600	155	0,9	139
	800	120	0,9	
	630	139	0,7	142
$TiCl_3 3Dioxan$	350	155	0,9	139
	450	120	0,9	
	440	147	0,7	142
	130	130	0,75	145
	—260	130	0,75	
$TiCl_3 3\gamma$-pic	520	130	0,7	145
$TiCl_3 3/2(CH_2OCH_3)_2$	540	90	0,85	145
$TiBr_3 2[(CH_3)_3N]$	260	130	0,6	145
$Ti(acac)_3$	7500	150	1,0	51
Cs_2VCl_6	130	130	0,85	146
$(pyH)_2VCl_6$	150	150	0,75	146
$(quinH)_2VCl_6$	320	160	0,8	146
	340	170	0,85	
$(pyH)_2VOCl_4$	2040	170	1,0	146
	1300	130	0,8	
$(pyH)_2VOCl_4$ $2H_2O$	2880	240	1,0	146
	1120	140	0,65	
$(quinH)_2VOCl_4$	2160	180	1,0	146
	1080	120	0,7	
$[(C_2H_5)_4N]_2MoCl_6$	700	390	1,0	147
Cs_2MoOCl_5	1760	220	0,95	147
	1260	180	0,8	
Cs_2MoOBr_5	1000	100	1,0	147
	600	80	0,8	
$[(C_2H_5)_2H_2]NWBr_6$	960	1200	0,9	147
	660	1100	0,7	
WBr_5	1800	2000	0,8	147
	1400	1500	0,5	
Cs_2WOBr_5	1800	600	1,0	147
	1500	600	0,7	
Rb_2WOCl_5	2100	400	1,0	147
	1000	600	0,6	
$[(C_6H_5)_4As]WOCl_4H_2O$	8280	1800	1,0	147
	2800	1000	0,5	
$(quinH)_2WOCl_4$	7680	2400	0,85	147
	4800	1600	0,8	
$(quinH)_2WOBr_4$	3750	1000	1,0	147
	2000	1500	0,7	

Footnotes see Table 1.

7, indicate that Δ is generally larger for the second and third row transition metals than for the first row ones. This is in agreement with the data on Ru^{III} and Os^{III} complexes in Table 6. It also appears that the later transition series metals experience a greater reduction in λ and increase in electron delocalisation indicative of an increase in covalent bonding. Since neither structural data nor single crystal magnetic data have been reported for any of these complexes, the interpretation of the powder susceptibility results should be treated with caution.

The metal with a d^9 configuration most likely to form a series of tetrahedral complexes is copper(II). Unfortunately many of its complexes display magnetically concentrated behaviour[28] which makes their susceptibilities unsuitable for interpretation in favour of the symmetry of the complex. Also copper(II) has a large spin-orbit coupling constant ($\lambda o = -850\ cm^{-1}$) thus if $\Delta \simeq \lambda$ then Δ is no longer a small perturbation with respect to the cubic field operator since for tetrahedral complexes $10Dq \simeq 5000\ cm^{-1}$. Together these facts render many copper(II) complexes unsuitable for the theoretical treatment considered here. No attempt appears to have been made to interpret the magnetic studies of copper(II) tetrahedral complexes in this way.

(v) *Complexes with E ground terms*

A ^2E ground term arises from the configurations d^1 in tetrahedral symmetry, d^9 and d^7 spin-paired in octahedral symmetry. There is also the ^5E ground term to consider; this occurs for d^4 in octahedral and d^6 in tetrahedral symmetry. Since E terms correspond to a non-magnetic doublet in cubic symmetry information concerning the axial field splitting is not expected from magnetic susceptibility measurements apart from the second order term in spin-orbit coupling which contributes to the g tensor. The other means of estimating Δ is from variable temperatu Mössbauer spectra which at present limits the discussion to tetrahedral iron(II) complexes. Some values of Δ relating to the axial field splitting for the ^5E term are reported in Table 8.

All of the values of Δ reported in Table 8 are positive implying that the d_z^2

TABLE 8

FITTING PARAMETERS OBTAINED FOR SOME TETRAHEDRAL IRON(II) COMPLEXES

Complex	$\Delta\ (cm^{-1})$	$\lambda\ (cm^{-1})$	k	*Ref.*
$[(C_2H_5)_4N]_2FeCl_4$	135	−103	1,0	149
	±185	−103	1,0	150
$[(CH_3)_4N]_2FeCl_4$	125	−103	1,0	149*
$(PQ)FeCl_4$	470	−103	1,0	149
$[(C_2H_5)_4N]_2FeBr_4$	96	−103	1,0	149
$[(CH_3)_4N]_2Fe(NCS)_4$	101	−103	1,0	149
$(Cat)Fe(NCSe)_4$	292	−103	1,0	149

Footnote see Table 1.

orbital lies below the $d_x2_{-y}2$ and that a compression of the tetrahedron along the z axis has occurred. The largest distortions are observed for the two complexes with large flat cations, PQ and CaT, indicating that solid state effects as well as Jahn–Teller effects contibute to Δ in these complexes. With the exception of $[(C_2H_5)_4N]_2FeCl_4$ Δ appears to be independent of temperature and is possibly due to electronic effects arising from the Jahn–Teller theorem. However the effects of covalency and distortions produced by the surrounding lattice have not been included.

In conclusion it should be mentioned that direct transitions between the levels separated by Δ are possible in principle for many of the complexes studied. But without single crystal structural data the polarised spectra necessary for the unambiguous assignment of Δ have not been performed. In general the axial field splitting of orbitally degenerate ground terms is smaller than in the excited terms of the same molecule. Until more precise data become available from extensive experimental and structural studies the values of Δ reported here should not be interpreted too literally but in most cases general trends are significant.

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