Magnetic Properties Near the $^5T_2$ - $^1A_1$ Crossover

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When a d^6 transition metal ion is in an octahedral or pseudo-octahedral crystal field of suitable strength, the zero-point energies of the two possible ground states, $^5T_2$ and $^1A_1$, may be sufficiently close to permit appreciable populations of both states at temperatures accessible in the laboratory. In such a situation, the magnetic moments exhibit a marked temperature dependence, and differ markedly from those expected when only one of the states is appreciably populated. The magnetic properties expected near the "crossover" of the $^5T_2$ and $^1A_1$ states are described from a theoretical view point, and the approximations made are discussed in detail. By way of example, the magnetic behaviour of a series of ferrous complexes, believed to lie near the $^5T_2$-$^1A_1$ crossover, are examined, and estimates of the separation of the two states are made for each of the complexes by comparison of the observed magnetic behaviour with the theory.

Introduction

The calculations of Tanabe and Sugano[1] have shown that a d^6 ion in a crystal field can have either a quintet (four unpaired electrons) or a singlet (no unpaired electrons) ground state, depending on whether the crystal field interaction is weak or strong. In special cases where the crystal field is intermediate in strength, the quintet ($^5T_2$) and the singlet ($^1A_1$) states may be nearly equienergetic, and the d^6 ion is said to lie near the «crossover» of the $^5T_2$ and $^1A_1$ states.

Iron(II) has a d^6 configuration, and complexes in which it has a $^5T_2$ ground state («high spin») are well known, as are those with a $^1A_1$ ground state («low spin»).[2-4] An attempt[5] to interpret the magnetic properties of the complexes $[FeL_2X_2]^\circ$ (L=phenanthroline or dipyridyl, X=NCS, NCSe) in terms of the $^5T_2$-$^1A_1$ crossover was unsuccessful.[6] Subsequently, a group of complexes very similar to these was found to have properties characteristic of the crossover.[7] More recently a series of anionic[8] and uncharged[9]

ferrous complexes with tridentate ligands were reported to have anomalous magnetic properties suggestive of the crossover situation. It is this latter group of complexes that we will use to illustrate the treatment given below for the $^5T_2$–$^1A_1$ crossover.

Theory

The isomorphism of the $^{2S+1}P_J$ with the $^{2S+1}T_1$ and $^{2S+1}T_2$ states[10,11,12] transforms the spin-orbit coupling-magnetic field interaction Hamiltonian

$$\varkappa = \sum_i \zeta l_i \cdot s_i + \sum_i \beta(l_i + 2s_i) \cdot H \qquad (1)$$

for Russel-Saunders coupling into a new Hamiltonian

$$\varkappa = \nu L \cdot S + \beta(\gamma L + 2S) \cdot H \qquad (2)$$

The eigenfunctions $\Psi(JM)$ of the Hamiltonian (2) are then related to the eigenfunctions $|LSM_LM_S\rangle$ for the Hamiltonian (1) by the Clebsch-Gordan coefficients $\langle LSM_LM_S|LSJM\rangle$ in the equations

$$\Psi(JM) = \sum_{M_LM_S} \langle LSM_LM_S|LSJM\rangle|M_LM_S\rangle$$

Thus we obtain the wavefunctions $|\Psi(^5T_2)\rangle$ from the functions $|1\ 2\ M_LM_S\rangle$ in the state $|t_2^4(^3T_1)e^2(^3A_2)^5T_2\ 1\ 2\rangle$.

Operation with Hamiltonian (2) on $|\Psi(^5T_2)\rangle$ now yields the eigenvalues

$E_1 = 2\nu + bH - 8aH^2/27$

$E_2 = 2\nu + \dfrac{2}{3}bH - 8aH^2/27$

$E_3 = 2\nu + \dfrac{1}{3}bH - 8aH^2/27$

$E_4 = 2\nu - 8aH^2/27$

$E_5 = 2\nu - \dfrac{1}{3}bH - 8aH^2/27$

$E_6 = 2\nu - \dfrac{2}{3}bH - 8aH^2/27$

$E_7 = 2\nu - bH - 8aH^2/27$

$E_8 = -\nu + 2cH - 5aH^2/27$

$E_9 = -\nu + cH - 5aH^2/27$

$E_{10} = -\nu - 5aH^2/27$

$E_{11} = -\nu - cH - 5aH^2/27$

$E_{12} = -\nu - 2cH - 5aH^2/27$

$E_{13} = -3\nu + \dfrac{6-\gamma}{2}\beta H + aH^2$

$E_{14} = -3\nu + aH^2$

$E_{15} = -3\nu + \dfrac{\gamma-6}{2}\beta H + aH^2$

where $a = (\gamma - 1 - \gamma^2/4)\beta^2/\nu$

$b = (4 + \gamma)\beta$

$c = (10 + \gamma)\beta/6 \qquad (3)$

(1) Y. Tanabe and S. Sugano, *J. Phys. Soc.*, (Japan), 9, 776 (1954).
(2) B. N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, 6, 37 (1964).
(3) H. R. H. Patil, Ph. D. Thesis, University of New South Wales (1967).
(4) E. Sinn, Ph. D. Thesis, University of New South Wales (1968).
(5) E. König and K. Madeja, *Chem. Commun.*, 61 (1966).
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(8) R. N. Sylva and H. A. Goodwin, *Australian J. Chem.*, 20, 479 (1967).
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If the value of the crystal field parameter Δ (the «ligand field strength») and a point group corresponding closely to the actual symmetry are both known for a particular complex, the wavefunctions can be derived quite accurately from first principles by a fairly straightforward, though tedius, calculation,[1,11,12] including such factors as configurational mixing and metal-ligand bonding. The values of ν and γ then result from operation with the first two terms of Hamiltonian (2). The dependence of ν on mixing and bonding effects can then be incorporated in a constant k, where $\nu = \dfrac{k\zeta}{2S}$, ζ ($=-4\lambda$) being the free ion one-electron spin-orbit coupling constant. We will follow an alternative procedure, and equate $\nu = -\dfrac{\gamma\zeta'}{2S}$, where ζ' ($=-\dfrac{k\zeta}{\gamma}$) is the effective spin-orbit coupling constant in the complex under consideration. Then in estimating ν theoretically or experimentally, we are estimating the deviation of spin-orbit coupling constant, ζ', from the free ion value, ζ. The value of γ likewise depends on the ligand field strength.

By equating the matrix elements $\langle\Psi(^5T_2)|\lambda\mathbf{L}\cdot\mathbf{S}+\beta(\mathbf{L}+2\mathbf{S})\cdot\mathbf{H}|\Psi(^5T_2)\rangle$ and $\langle\Psi(^5T_2)|\nu\mathbf{L}\cdot\mathbf{S}+\beta(\gamma\mathbf{L}+2\mathbf{S})\cdot\mathbf{H}|\Psi(^5T_2)\rangle$ for a pure $^5T_2$ term (i.e. when there is no mixing with other states, all bonding coefficients $=1$, $\zeta'=\zeta$, and $|\Psi(^5T_2)\rangle=|t_2^4(^3T_1)e^2(^3A_2)\rangle$), the values $\gamma=-1$ and $\nu=\zeta/4$ are obtained.

When the value of Δ, and the bonding coefficients are unknown, γ and ζ' cannot be calculated. One possible procedure would be to perform the calculation at a specific value of Δ, to obtain results which would be reasonable approximations to the real situations in specific complexes, for which Δ is known to be sufficiently close to the assumed value. Thus detailed calculations have been performed exactly at the $^6A_1$–$^2T_2$ crossover,[13] and applied to the ferric dithiocarbamates, which generally lie near to the crossover.[14,15] Such a calculation gives the maximum possible mixing of states. This calculation did not include the bonding coefficients, which have only minor effects on the magnetic properties, though their inclusion in the theory would not lead to difficulty.

An alternative procedure would be to estimate the values of γ and ν (or γ and ζ') from the comparison of calculated and experimental results. If E is the separation of the zero-point energies of the $^5T_2$ and $^1A_1$ states, then the magnetic properties near the crossover of these two states is represented by a Boltzmann distribution over the eigenvalues of the two states. Thus, if the zero-point energy of the $^5T_2$ state is taken as origin, the single eigenvalue (E_o) in the $^1A_1$ state is equal to $-E$. The two crossing states are now represented by 16 eigenvalues E_i, where $E_o=-E$ and the other 15 values are given by (3).

(13) J. M. de Lisle and R. M. Golding, *Proc. Roy. Soc.* (London), A **296**, 457 (1967).
(14) A. H. Ewald, R. L. Martin, I. G. Ross, and A. H. White, *Proc. Roy. Soc.* (London), A **280**, 235 (1964).
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Using the 16 eigenvalues in the relation

$$\mu^2_{eff} = -\frac{3kT}{\beta^2} \times \frac{\sum\limits_{i=0}^{16} \dfrac{\delta E_i}{\delta H} e^{-E_i/kT}}{\sum\limits_{i=0}^{16} e^{-E_i/kT}}$$

and assuming $\beta H \ll kT$, we have, for the magnetic properties near the $^5T_2$–$^1A_1$ crossover,

$$\mu^2_{eff} = \{56[3\gamma x(4+\gamma)^2+16(1-\gamma/2)^2]e^{\gamma x/2}+5[3\gamma x(10+\gamma)^2+80(1-\gamma/2)^2]e^{-\gamma x/4}+27[\gamma x(6-\gamma)^2-48(1-\gamma/2)^2]e^{-3\gamma x/4}\}/\{18\gamma x[7e^{\gamma x/2}+5e^{-\gamma x/2}+3e^{-3\gamma x/4}+Ce^{E/kT}]\}$$

(4)

where $x=\zeta'/kT$, and C is discussed below. Assuming for the moment that $C=1$, we investigate the effect of reasonable variations in γ and ζ', using as limits the pure $^5T_2$ value of $\gamma=-1$, and the free ion value of $\zeta'=400$ cm^{-1}. Figure 1 shows how the magnetic properties, as calculated, depend on such variations in γ and ζ'. A glance at the experimental results[8,9] to be used as an illustration of the magnetic properties near the crossover, shows that variations in γ and ζ' have a smaller effect on the shapes of the theoretical curves than the experimental scatter has on the shapes of the experimental curves.

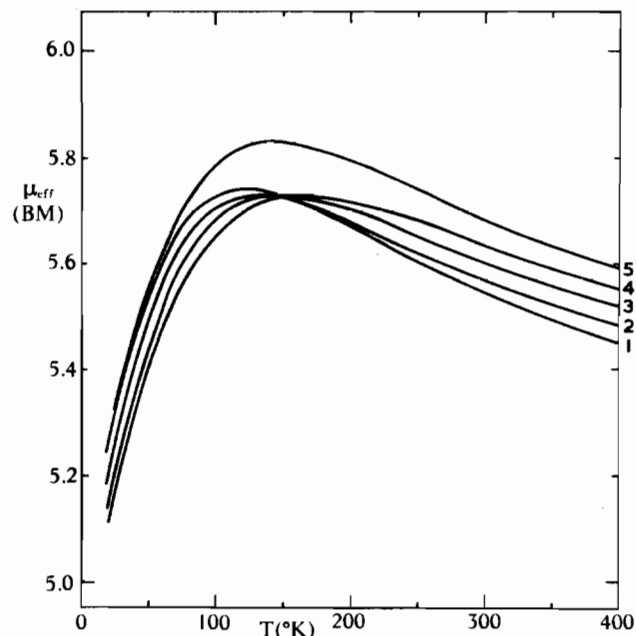Figure 1. Temperature dependence of μ_{eff} in the $^5T_2$ state ($E\ll O$) calculated from equation (4) using values $\gamma=-1$, $\zeta'=280$ cm^{-1} (curve 1); $\gamma=-1$, $\zeta'=320$ cm^{-1} (curve 2); $\gamma=-1$, $\zeta'=360$ cm^{-1} (curve 3); $\gamma=-1$, $\zeta'=400$ cm^{-1} (curve 4); $\gamma=-1.1$, $\zeta'=320$ cm^{-1} (curve 5).

As the theoretical curves are not very sensitive to the values chosen (whether on a theoretical or an experimental basis), the main features of the magnetic properties near the $^5T_2$–$^1A_1$ crossover are represented by equation (4) for any reasonable values of γ and ζ'. We will assume values of $\gamma=-1$ and $\zeta'=320$ cm^{-1}.

Vibrational Partition Functions

The dependence of the crystal field interaction V(r) on the metal-ligand distance, a, is given by the relation

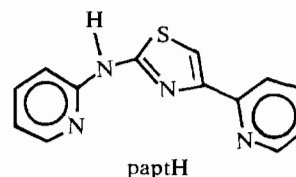$$V(r) = e^2 Z \langle r^4 \rangle f / a^5 = 3\Delta 5$$

Here f is a number depending on the particular point group representation for the complex, and is determined from group theory considerations; r relates to the electron distribution, and should not be confused with a, though the two are necessarily related to a considerable extent. The transfer of electrons from the t_2 orbital subset to the e subset is expected[16] to increase a, and therefore to decrease Δ.[17] This phenomenon has been confirmed experimentally in the case of the $^6A_1$–$^2T_2$ crossover in ferric dithiochelates, where the low spin species were found from pressure- dependent studies to occupy a smaller volume than the high spin.[14,15,18] From this it was deduced[14] that the inequality Δ(high spin)$<\pi<\Delta$(low spin) where π is the electron pairing energy, must hold for the crossover, and that the vibrational partition functions for the two states should be different. The need to include the vibrational partition functions has become apparent in the interpretation of the temperature dependence of the magnetism of solid ferric dithiochelates[14,15] and from comparison of the solution magnetic moments with the NMR contact shifts.[19] Such an abundance of experimental evidence is not yet available for the $^5T_2$–$^1A_1$ crossover, but it is apparent that a similar situation should apply.

The temperature dependence of the partition function ratio, $C=Q_A/Q_T$ (where Q_A, Q_T refer to the $^1A_1$ and $^5T_2$ states respectively) can be approximated by $Q_A/Q_T = Q_o e^{-Q_1/kT}$ over the temperature range of interest (100-400°K). While Q_A, Q_T, Q_o, Q_1 cannot be known with any precision, order of magnitude calculations indicate that values $Q_o \sim 10^{-1}$ and $Q_1 \sim -30$ cm^{-1} would be reasonable. Thus the temperature dependence of C has the effect of increasing E by a small amount Q_1, of the order of 30 cm^{-1}, a negligible error in the present context. At this stage we will estimate C from the optimal fit of the experimental data to equation (4), keeping in mind that this method will incorporate into C all the weighting factors other than the degeneracy that should be applied to the Boltzmann factors (such as distortion from octahedral geometry, lattice forces, configurational mixing, etc.). The ratio of the vibrational partition functions is only one of these, though undoubtedly the largest.[14,15]

Comparison with Experiment

Sylva and Goodwin[8] have reported that ferrous complexes Fe(paptH)$_2^{2+}$ with the ligand 2-(pyridyl-

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(17) C. K. Jørgensen, «Absorption Spectra and Chemical Bonding in Complexes», Oxford, Pergamon Press (1962).
(18) A. H. Ewald and E. Sinn, Australian J. Chem., 21, 927 (1968).
(19) R. M. Golding and W. C. Tennant, J. Chem. Phys., in press.
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amino)-4-(2-pyridyl)thiazole[20] (paptH) have temperature dependent

paptH

magnetic moments which are generally intermediate between high and low spin. The ferrous complexes [Fe(papt)$_2$] of the deprotonated ligand was found to behave similarly.[9] It was suggested,[8,9] from a qualitative viewpoint, that these properties could arise from the $^5T_2$–$^1A_1$ crossover. Figure 2 compares the experimental results,[8] for the Fe(paptH)$_2^{2+}$ complexes with the μ_{eff} (T) curves calculated from equation (4), using the values of E and C listed in Table I. Constant values of -1 and 320 cm^{-1} were used throughout for γ and ζ' respectively.
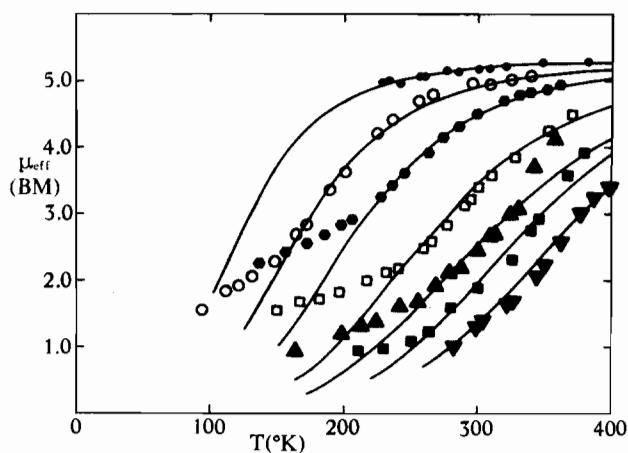

Figure 2. Temperature dependence, obtained from refs. 8, 9, of the magnetic moment μ_{eff} of the complexes: ▼, Fe(paptH)$_2$Br$_2$.2H$_2$O; ■, Fe(paptH)$_2$Cl$_2$.2H$_2$O; ▲, Fe(paptH)$_2$(NO$_3$)$_2$.H$_2$O; □, Fe(paptH)$_2$SO$_4$.5H$_2$O; ●, Fe(paptH)$_2$(NCS)$_2$.H$_2$O; O, [Fe(papt)$_2$]; ●, Fe(paptH)$_2$(NO$_3$)$_2$. The full curves are calculated from equation (4), using the values of E and C given in Table 1; values of 320 cm^{-1} and -1.0 were used for ζ' and γ in each case.

Table I. Estimated Values of E and C for Fe(paptH)$_2^{2+}$ Complexes

Complex	E (cm^{-1})	C
Fe(paptH)$_2$Br$_2$.2H$_2$O	2010	0.02
Fe(paptH)$_2$Cl$_2$.2H$_2$O	1760	0.03
Fe(paptH)$_2$(NO$_3$)$_2$.H$_2$O	1400	0.09
Fe(paptH)$_2$SO$_4$.5H$_2$O	1250	0.09
Fe(paptH)$_2$(NCS)$_2$.H$_2$O	1000	0.08
Fe(paptH)$_2$(NO$_3$)$_2$	620	0.15

While the agreement at high temperatures is reasonable, that at low temperatures is not. This is not surprising, since none of the experimental curves extrapolate through the origin, or to any other point; most of them tend to an arbitrary, constant paramagnetic μ_{eff} value at low temperatures, suggesting the presence of some purely high spin material.

Paramagnetic Impurities

In a low spin iron(II) complex, the effect of small amounts of paramagnetic impurities can be quite startling: the zero or near zero μ_{eff} value can be raised above 1.0 B.M. if as little as 3% of the iron(II) is replaced by iron(III). Such quantities of paramagnetic impurities cannot, in general, be detected by analytical methods. We[21] have examined the temperature dependence of the magnetic properties of a large range of low spin ferrous complexes with nitrogenous ligands for which moments of the order of 1.0-2.0 B.M. had been reported.[22,23] In each case we found this magnetism to result from the presence of paramagnetic impurities, with negligible contribution from the temperature independent paramagnetism which is expected from the mixing of the $^1A_1$ and $^3T_1$ states. If the ligands (LH) in such complexes are readily deprotonated (to L), then a ferrous complex of the type $Fe(LH)_2X_2$ might contain a considerable proportion of the ferric complex $[Fe(LH)L]X_2$, and the analytical purity of the complex would be very little affected. Deprotonation reactions are well known in such ligands as PAPHY[23] and paptH.[8,9,20]

The magnetic properties of the $Fe(paptH)_2^{2+}$ complexes at low temperatures need not be due to the presence of paramagnetic impurities, for it has been shown that the complexes generally may exist in more than one form with differing magnetic properties in the different forms, and transformation between them is induced by heating, recrystallisation and in some cases by cooling.[8] Thus a complex in which μ_{eff} is temperature dependent can be converted by heating into a purely high spin form without chemical change.[8] It is therefore quite likely that various proportions of permanently high spin material are present in the complexes («permanently» is here used in a relative sense, for it has been found that at constant low temperatures slow phase transitions may occur in some of these complexes, accompanied by an appreciable drop in μ_{eff} over a period of several hours).[8] The proportion of permanently paramagnetic material, p, (assumed to be a high spin modification of the same complex) in each complex was estimated from the low temperature limit of μ_{eff}, and the new E, C values are given in Table II. Figure 3 compares the experimental results and the new calculated μ (T) curves. The correlation is now seen to be good, and the postulate of Goodwin and Sylva is verified. The effect on E of correcting for paramagnetism is surprisingly small, but there is a larger effect on C.

We therefore have a useful method of estimating the separation E, the most important quantity in a crossover situation, and the validity of the general method is apparent. The accuracy available for C and ζ' is necessarily poorer. We have adopted the procedure of keeping ζ' constant for the entire series of complexes, since magnetic susceptibility measurements alone could not reasonably be used to estimate both C and ζ'. If the treatment were refined to include the mixing of states, and more accurate values of ζ' and C, then it would become desirable to include a number of other small effects. Distortion from octahedral symmetry, the effect of bonding to the ligands, and the effects of the anions, the water of crystallisation and of the lattice surrounding each molecule, should be taken into account.
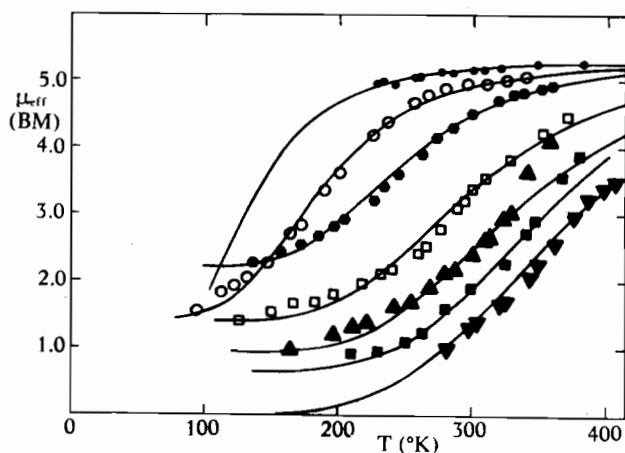

Figure 3. Magnetic properties of the iron(II) complexes described in Figure 1. The full curves are calculated from equation (4) modified to take account of the «paramagnetic impurities». The values of p, E, and C used in the calculations are given in Table II; values of 320 cm⁻¹ and —1.0 were used for ζ' and γ in each case.

The effect of distortion is not readily estimated without structural information, such as single crystal X-ray data, or even EPR spectra. As an approximation, we could add a distortion term to the Hamiltonian, and consider, for example, an octahedral complex with tetragonal distortion. Calculations of this type have been made in some situations[24-28] and the effect of the distortion on μ_{eff} is often surprisingly small. The effect of bonding to the ligands becomes important only when the orbital contribution to μ_{eff} is large compared to the spin contribution, and may reasonably be ignored in the present approximation.

An effect which will be important is the anion effect. Again, this could be incorporated into the Hamiltonian, given the distances of the anions from the iron atoms, and the charge distribution over the anions. The effect of waters of crystallisation could

Table II. Values of p, E, and C for $Fe(paptH)_2^{2+}$ Complexes

Complex	p (%)	E (cm⁻¹)	C
$Fe(paptH)_2Br_2 . 2H_2O$	0	2010	0.024
$Fe(paptH)_2Cl_2 . 2H_2O$	1.65	1850	0.07
$Fe(paptH)_2(NO_3)_2 . H_2O$	2.97	1500	0.08
$Fe(paptH)_2SO_4 . 5H_2O$	6.61	1300	0.07
$Fe(paptH)_2(NCS)_2 . H_2O$	16.5	1100	0.15
$Fe(paptH)_2(NO_3)_2$	0	620	0.02

(21) C. M. Harris and E. Sinn, to be published.
(22) B. N. Figgis and J. Lewis, Progr. Inorg. Chem., 6, 37 (1964).
(23) J. F. Geldard and F. Lions, Inorg. Chem., 2, 270 (1963).

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(25) B. N. Figgis, Trans. Faraday Soc., 57, 204 (1961).
(26) B. N. Figgis, J. Lewis, F. E. Mabbs, and G. A. Webb, J. Chem. Soc. (A), 442 (1967).
(27) R. M. Golding, K. F. Mok, and J. F. Duncan, Inorg. Chem., 5, 774 (1966).
(28) E. König and A. S. Chakravarty, Theoret. Chim. Acta, 9, 151 (1967).

be included on the basis of an electric dipole model, but again, detailed structural information would be required. Clearly, the change in magnetic properties (and hence in E, C, and ζ') from compound to compound is largely due to the effect of the anions and water of crystallisation. The lattice effect must be related to these effects, and probably could not be treated separately. The phase changes which occur in many of the complexes reflect changes in the lattice, which probably include alterations of the relative dispositions of the cations, anions and waters. In the absence of complete structural information,

these influences can only be qualitatively noted, and not estimated quantitatively.

The complex $[Fe(papt)_2]$ represents a physically much simpler situation than the other complexes, and does not appear to exhibit any phase changes.[9] The temperature dependence of μ_{eff} is quite well represented by equation (4) when $E=790$ cm^{-1} and $C=0.13$. The fit is further improved (Figure 3) by taking permanently paramagnetic species into account ($E=830$ cm^{-1}, $C=0.11$ and $p=6.6\%$). Thus the behaviour of this complex, like that of the cationic complexes, is in keeping with a crossover situation.