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Apparently Anomalous Magnetism in Low Spin Iron(II) Complexes

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A systematic investigation of some iron(II) complexes which might be expected to lie near the high spin — low spin crossover, shows that the complexes are actually low spin, and previously reported anomalous magnetic moments are found to arise essentially from paramagnetic impurities. The temperature independent paramagnetism (χ^*) expected for iron(II) in the low spin ($^1A_1$) state is calculated and the utility of comparison with available results of electronic absorption and Mössbauer Effect spectroscopy measurements discussed. The approximations involved in calculations of χ^* are discussed in detail, and the maximum value of χ^* that could reasonably be expected is estimated at 3×10^{-4} c.g.s.e.m.u. This estimate is supported by experimental magnetic susceptibility measurements which may be reasonably explained in terms of a value of χ^* less than 3×10^{-4} c.g.s.e.m.u., together with, in some cases, a contribution from a paramagnetic impurity with normal Curie-Weiss behaviour. Where applicable, the magnitude of the contribution from paramagnetic impurities is estimated.

Introduction

Many iron(II) complexes have been reported with magnetic moments intermediate between the high spin ($\sim$5 B.M.) and the low spin ($<$1 B.M.) values,[1-13] and many of these were found to be temperature dependent. In some cases, the moment rises sharply from low spin to high spin values over a range of a few °C,[5-8] which can only be ascribed to a solid phase transition. In other cases, a more gradual rise of the magnetic moments with temperature[9-13] is compatible with a « crossover » situation, where the high spin ($^5T_2$) and the low spin ($^1A_1$) states are nearly equienergetic,[12] or with antiferromagnetic exchange interactions between the neighbouring iron atoms.[14] As has been pointed out,[2] paramagnetic impurities in a low spin ferrous complex could account for an anomalous magnetic moment; in fact, a zero or near-zero magnetic moment can be raised above 1.0 B.M. if as little as 3% of the iron(II) is replaced by iron(III), but the moment should then be temperature independent. Thus the temperature dependence of these anomalous magnetic moments can be used to determine the origin of the anomaly. In a low spin complex, there is also a small intrinsic paramagnetism which must be taken into consideration.

Theory

Of the mechanisms giving rise to anomalous magnetic moments in ferrous complexes, the $^5T_2$ - $^1A_1$ crossover has previously been described,[12] and the intrinsic paramagnetism in the low spin state is discussed in detail below. The effect of paramagnetic impurities can then be estimated from experimental results.

Paramagnetism in the Low Spin d^6 Ion. Tanabe and Sugano[15] have determined the complete crystal field - electrostatic interaction matrix for the d^6 Co^{3+} ion in a crystal field of octahedral symmetry. Their calculation may be applied to the d^6 Fe^{2+} ion, though the values of the ligand field strength Δ, and the Racah parameters B and C are different.[16-18] Figure 1 shows the dependence of the lowest lying excited states in the Fe^{2+} ion on Δ.

When configurational mixing is included, the wavefunction of the $_1A^1$ state is given, in the notation of Griffth[16] by

$$\begin{aligned} |{}^1A_1\rangle = {} & a\,|t_2^6\rangle + b\,|t_2^4({}^1E)e^2({}^1E)\rangle + c\,|t_2^4({}^1A_1)e^2({}^1A_1)\rangle + \\ & + d\,|t_2^3({}^2E)e^3({}^2E)\rangle + e\,|t_2^2e^4\rangle \end{aligned} \tag{1}$$

where a, b, ... e are coefficients dependent on Δ and may be obtained from the crystal field - electrostatic in-

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(1) S. Sugden, *J. Chem. Soc.*, 328 (1943).
(2) B. N. Figgis and J. Lewis, Progr. *Inorg. Chem.*, *6*, 37 (1964).
(3) J. F. Geldard and F. Lions, *Inorg. Chem.*, *2*, 270 (1963).
(4) H. A. Goodwin, *Australian J. Chem.*, *17*, 1366 (1964).
(5) W. A. Baker and H. M. Bobonich, *Inorg. Chem.*, 3, 1184 (1964).
(6) E. König and K. Madeja, *Chem. Commun.*, 61 (1966).
(7) E. König and K. Madeja, *Inorg. Chem.*, 6, 48 (1967).
(8) E. König, K. Madeja, and. K. J. Watson, *J. Amer. Chem. Soc.*, *90*, 1146 (1968).
(9) C. M. Harris, R. L. Martin, H. R. H. Patil, and E. Sinn, paper presented at the 39th A.N.Z.A.A.S. Congress, University of Melbourne, Jan. 1967.
(10) R. N. Sylva and H. A. Goodwin, *Australian J. Chem.*, *20*, 479 (1967).
(11) R. N. Sylva and H. A. Goodwin, *Australian J. Chem.*, *21*, 1081 (1968).
(12) C. M. Harris and E. Sinn, *Inorg. Chim. Acta*, *2*, 296 (1968).
(13) J. P. Jesson, S. Trofimenko and D. R. Eaton, *J. Amer. Chem. Soc.*, *89*, 3158 (1967); J. P. Jesson, J. F. Weiher and S. Trofimenko, *J. Chem. Phys.*, *48*, 2058 (1968).
(14) A. L. Balch, I. G. Dance, and R. H. Holm, *J. Amer. Chem. Soc.*, *90*, 1139 (1968); I. G. Dance and R. H. Holm, to be published.
(15) Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, *9*, 753 (1954).
(16) J. S. Griffith, « The Theory of Transition-Metal Ions », Cambridge University Press, 1961.
(17) R. M. Golding, « Applied Wave Mechanics », van Nostrand, London, 1969.
(18) C. J. Ballhausen, « Introduction to Ligand Field Theory », McGraw-Hill Book Co., London, 1962.
(19) Ref. 16, App. 2.

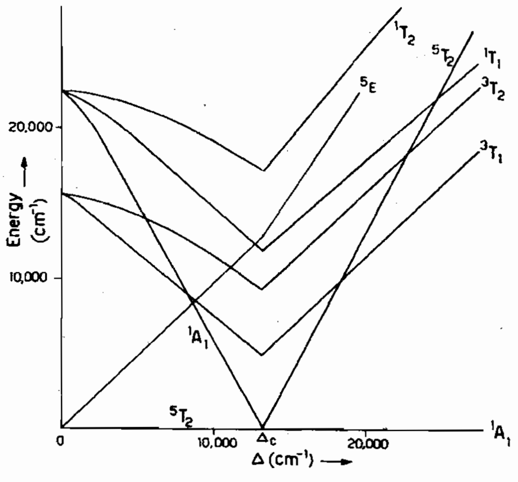

Figure 1. Energies of the lowest lying excited states, for Fe^{2+} in an octahdral ligand fild, as a function of the ligand field strength Δ. B(=C/4) is taken as 700 cm^{-1} and ζ as 350 cm^{-1}.

teraction matrix,[19] and it is found that $0.97 < a < 1$ while the other coefficients are quite small. Thus the wavefunction is approximately given by $|t_2^6\,{}^1A_1>$. There is no first order magnetic moment in this state, since $<t_2^6\,{}^1A_1|\sum_{i=1}^{6}\beta(l_{iz}+2s_{iz})H|t_2^6\,{}^1A_1> = 0$. Thus the entire susceptibility arises from interactions of $|t_2^6\,{}^1A_1>$ with higher states$|\Psi_n>$ through the magnetic field interaction $\beta H\Sigma(l_{iz}+s_{iz})$. $\Sigma\, s_{iz}$ must be zero in $|t_2^6\,{}^1A_1>$ so that any interaction must be through $\sum_i l_{iz}$. l_z transforms as T_1 and only $^1T_1$ states give non-zero interaction matrix elements with $^1A_1$. The $^1T_1$ wavefunctions are given by

$$|{}^1T_1> = f|t_2^5e> + g|t_2^4({}^1T_2)e^2({}^1E)> + h|t_2^3({}^2T_1)e^3({}^2E)> + \\ + i|t_2^3({}^2T_2)e^3({}^2E)> \qquad (2)$$

In a strong field case $(\Delta > \Delta_c)$ g, h, i in (2) are negligible, so that the wavefunction is essentially $|t_2^5e\,{}^1T_1\,0>$ and in the complex notation[16] this is $-1/\sqrt{2}\{|(1^2-1^2\zeta_1^+\,\varepsilon^-)>+|(1^2-1^2\zeta_1^-\,\varepsilon^+)>\}$. The new to first order in H, is

$$|\psi> = |t_2^6\,{}^1A_1> + \frac{2\sqrt{2}\beta H\,|t_2^5e\,{}^1T_1 0>f}{E(t_2^5e\,{}^1T_1)-E(t_2^6\,{}^1A_1)+\delta_1} \qquad (1')$$

and the associated susceptibility is expressed by

$$\chi = \frac{16N\beta^2f^2}{E(t_2^5e\,{}^1T_1)-E(t_2^6\,{}^1A_1)+\delta_1} = 16N\beta^2f^2/E_1 \qquad (3)$$

Here δ_1 allows for configurational mixing within the two states, and the polarisation correction $67L(L+1)$ cm^{-1}.[16,20] When Δ is near to Δ_c, δ_1 is found from (1) - (3) to be about 2000 cm^{-1}. As Δ increases, $\delta_1 \rightarrow 0$. When f is equated to unity, and δ_1 to zero, (3) reduces to the equation given by Griffith.[16] Since there are non-zero matrix elements $<t_2^6\,{}^1A_1|\mathbf{l}_i\cdot\mathbf{s}_i|\Gamma>$ when $|\Gamma>$ is $|t_2^5e\,{}^3T_1>$, spin-orbit coupling interaction adds a term $\frac{6\zeta}{E(t_2^5e\,{}^3T_1)-E(t_2^6\,{}^1A_1)}|\Phi>$ to equation (1′), where ζ is the spinorbit coupling constant, and $|\Phi>$ a linear combination of $|1\ -1>$ $|-1\ 1>$ and $|0\ 0>$ of $|t_2^5e\,{}^3T_1>$. $<\Phi|\beta\sum_{i=1}^{6}(l_{iz}+2s_{iz})H|\Phi> = 0$ so that no first order contribution is added to χ in equation (3). Higher order contributions to χ from this term are negligible here.

Bonding Effects. The t_2 and e orbitals used in the calculations are not exactly d-orbitals due to bonding with the ligands,[16,17,21-26] and some allowance must be made for this. The simplest method is that outlined by Griffith,[16] leading to a corrected susceptibility χ^* given by

$$\chi^* = k\chi \qquad (4)$$

where k $(0<k<1)$ is called an orbital reduction factor and 1-k gives a measure of the deviation from pure d-orbital character, as a result of metal-ligand bonding. In low spin complexes, where bonding effects should be considerable, k values of the order or 0.6-0.8 seem the most reasonable.

Correlation with Electronic Spectra. Complexes in which the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition has been observed are now dealt with quite simply. In the low spin tris-chelated ferrous complexes of glyoxal-bis-N-methylimine (GMI), biacetyl-bis-N-methylimine (BMI) and biacetyl-bis-N-butylimine (BBI), the $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions have been assigned to absorptions near 25,000 and 28,000 cm^{-1} respectively,[27] so that from (4), $\chi^* \doteqdot 160k \times 10^{-6}$ c.g.s.u.

Since Δ must be greater than Δ_c in a low spin complex, it is possible to estimate maximum values for $1/E_1$ and hence χ^* in (3) and (4), in order to deal with the majority of low spin ferrous complexes for which neither spectral data nor Δ values are available. E_1 is related to Δ by

$$E_1 = \Delta - C + \delta_1 \qquad (5)$$

Estimates of Δ_c have varied slightly,[6,13,18] but its value is close to 13,000 cm^{-1}. An examination of the magnetic properties near the $^5T_2 - {}^1A_1$ crossover[12] indicates that significant high spin contribution should be observed in a temperature dependent magnetic study, unless the $|t_2^4e^2\,{}^5T_2>$ state is more than 2000 cm^{-1} above the $|t_2^6\,{}^1A_1>$ ground state. This means that, for low spin behaviour, Δ must be considerably more than 1000 cm^{-1} above Δ_c.

For the gaseous Fe^{2+} ion,[16] the value of C is 3900 cm^{-1} but in iron(II) complexes, C is considerably lower and may be estimated, rather approximately, in the compounds for which the $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions

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(20) R. E. Trees, *Phys. Rev.*, 83, 756 (1951).

(21) K. W. H. Stevens, *Proc. Roy. Soc. (London)* (A) *219*, 542 (1953).

(22) R. G. Shulman and S. J. Sugano, *J. Chem. Phys.*, *42*, 39 (1965).

(23) B. N. Figgis, *Trans. Faraday Soc.*, 57, 204 (1961).

(24) B. N. Figgis, J. Lewis, F. E. Mabbs and G. A. Webb, *J. Chem. Soc.* (A) 442 (1967).

(25) R. M. Golding and H. J. Whitfield, *Trans. Faraday Soc.*, *62*, 1713 (1966).

(26) R. M. Golding, *Mol. Phys*, *12*, 13 (1967).

(27) T. Ito, N. Tanaka, I. Hanazaki and S. Nagakura, *Bull. Chem. Soc. Japan*, *41*, 365 (1968); I. Hanazaki, F. Hanazaki and S. Nagakura, *J. Chem. Phys.*, to be published.

have been assigned, using equation (5) and the relation

$$E_2 = E(^1T_2)-E(^1A_1) = \Delta+16B-C+\delta_2 \qquad (6)$$

where δ_2 is a correction allowing for mixing and polarisation.[16,20]. The latter part of the correction is small, and the mixing contribution consists essentially of the lowering of the $|^1T_2>$ state below the $|t^5_2e\ ^1T_2>$, and this can be estimated from the relation

$$\begin{aligned}|^1T_2> = {} & j\,|t^5_2e> + k'\,|t^4_2(^1T_2)e^2(^1A_1)> + l\,|t^4_2(^1T_2)e^2(^1E)> + \\ & + m\,|t^4_2(^3T_1)e^2(^3A_2)> + n\,|t^3_2(^2T_2)e^3(^2E)> + \\ & + o\,|t^3_2(^2T_1)e^3(^2E) + p\,|t^2_2e^4> \end{aligned} \qquad (7)$$

The coefficients j, k′, . . . p may be obtained from the crystal field - electrostatic interaction matrix,[19] and to sufficient accuracy all but j and k′ may be taken as zero. Making the usual approximation $C \doteqdot 4B$, δ_2 is found to be of the order of $-6000\ cm^{-1}$ near the crossover. This is quite large but the value decreases rapidly as Δ increases. In the GMI, BMI and BBI complexes, $E_1 \sim 25{,}000\ cm^{-1}$ and $E_2 \sim 28{,}000\ cm^{-1}$,[27] so that $\Delta \sim 26{,}000\ cm^{-1}$ and $C \sim 2000\ cm^{-1}$. In other calculations B ($\doteqdot C/4$) has been estimated as 600 cm^{-1} in $Fe(phen)_3^{2+}$ (phen = 1,10-phenanthroline)[28] and 400 cm^{-1} in $Fe(CN)_6^{4-}$.[29] In a series of the isoelectronic low spin cobalt(III) complexes, for which spectral data are available, the calculated B values range from 400-700 cm^{-1}.[29] It therefore seems likely that C will generally be significantly smaller than 3000 cm^{-1} in low spin iron(II) complexes, so that from (5) $E_1 > 1300\ cm^{-1}$ and $\chi^* < 310k \times 10^{-6}$ c.g.s.u. Thus, the maximum temperature independent susceptibility to be expected in low spin iron(II) is about 3×10^{-4} c.g.s.u., which corresponds to a magnetic moment of about 0.8-0.9 B.M. at room temperature.

Correlation with Mössbauer Results: Distortion from Octahedral Symmetry and Anisotropy of Bonding. The matrix elements $<t^6_2\ ^1A_1|H_1|t^6_2\ ^1A_1>$ are zero for the distortion Hamiltonian (8)[16,17,26]

$$H_1 = \sum_{i=1}^{6}\left[\varepsilon_{\parallel} l^2_{iz} + \frac{\varepsilon_{\perp}}{2}(l^2_{i+} + l^2_{i-})\right] \qquad (8)$$

where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are distortion parameters. Thus distortion from octahedral symmetry does not affect the spherical $^1A_1$ state, other than to impose directional dependence upon k, but it will increase or decrease $E(t^5_2\ ^1T_1)$ by a quantity δ_1', which cannot be estimated without a knowledge of the degree of distortion and which must be added to the denominator of (3). This has the effect of making more approximate the quantity δ_1 in (3).

Marked anisotropy in k would require (4) to be replaced by a more complicated relation. The anisotropy can be estimated from experimental Mössbauer results, which show small quadrupole splittings for iron(II) complexes with BMI, GMI and unsubstituted and ring-substituted phen and dipy (dipy = 2,2′-dipyridyl) ligands.[30] For transition metal ions, the quadrupole splitting of a Mössbauer spectrum can be interpreted using the Hamiltonian (9), in the usual notation[16,17,26,31]

$$H_2 = \frac{e^2Q(1-\gamma_\infty)<r^{-3}>}{7I(I-1)}\sum_{i=1}^{6}\left\{(l_i\,.\,I)^2 + \frac{1}{2}(l_i\,.\,I) - 2I(I+1)\right\} \qquad (9)$$

The metal-ligand bonding may be taken into account[26] by replacing the pure (unbonded) t_2 wavefunctions

$$|1^\pm>, \qquad |-1^\pm>, \qquad |\zeta_1^\pm>$$

by the molecular orbital wavefunctions

$$\alpha|1^\pm>+\Phi_1, \qquad \alpha|1^\pm>+\Phi_2, \qquad \beta|\zeta_1^\pm>+\Phi_3$$

(Φ_1, Φ_2, Φ_3 are the appropriate ligand orbitals) so that we have two directionally dependent orbital reduction factors $k_\alpha = \frac{1}{2} + \frac{\alpha^2}{2}$ and $k_\beta = \frac{1}{2} + \frac{\beta^2}{2}$ The only non-zero matrix elements arising from the operation of the Hamiltonian (9) on these wavefunctions are $<^1A_1\ M_I|H_2|^1A_1\ M_I> = 2(\beta^2-\alpha^2)[3M_I^2-I(I+1)]$, and the expected quadrupole spliting ΔE_Q is given by

$$\Delta E_Q = \frac{4}{7}e^2Q(1-\gamma_\infty)<r^{-3}>(\beta^2-\alpha^2) \qquad (10)$$

$e^2Q(1-\gamma_\infty)<r^{-3}>$ is of the order of 9 mm/sec,[17,26] and ΔE_Q is about 0.3 mm/sec in substituted and unsubstituted phen complexes of iron(II)[30] (it is not known whether ΔE_Q is positive or negative). Thus $\beta^2-\alpha^2 \doteqdot 0.06$, and $k_\alpha \doteqdot k_\beta \doteqdot k$, *i.e.* the bonding is almost completely isotropic. The largest ΔE_Q value observed in a range of fourteen iron(II) complexes with bi- and tri- dentate ligands was 1.14 mm/sec for $(Fe(terpy)_2^{2+}$ (terpy = 2,2′,2″-terpyridyl). In this case $\beta^2-\alpha^2 \doteqdot 0.2$ and $k_\beta - k_\alpha \doteqdot 0.1$, an anisotropy smaller than the accuracy to which k is known a priori, and no modification of (4) is warranted. More approximate estimates of χ^* have also been made[32] in cobalt(III) d^6 complexes.

It is apparent from (10) that while the directional dependence may be estimated, no absolute k values can be obtained from Mössbauer quadrupole splittings. Combination of magnetic susceptibilities and electronic spectra via (3) and (5) can give at best very approximate values for k. Independent estimates of k, though again approximate, can be made from NMR chemical shifts,[33] but no suitable experimental results are available at present.

Paramagnetic Impurities. The most likely paramagnetic impurities to be found in low spin ferrous complexes would be some high spin iron(II)[34] or iron(III) species. Small admixtures of high spin cobalt(II) species would have the same effect on low spin cobalt(III) complexes. The magnetic properties of such impurities could be adequately represented by a Curie-

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(28) K. Madeja and E. König, *J. Inorg. Nucl. Chem.*, *25*, 377 (1963).

(29) C. K. Jørgensen, « Absorption Spectra and Chemical Bonding in Complexes », Pergamon Press, London, 1962.

(30) L. M. Epstein, *J. Chem. Phys.*, *40*, 435 (1964).

(31) R. M. Sternheimer, *Phys. Rev.*, 95, 736 (1954).

(32) C. J. Ballhausen and R. W. Asmussen, *Acta Chem. Scand.*, *11*, 479 (1957).

(33) G. P. Betteridge and R. M. Golding, to be published.

(34) W. A. Baker and R. I. Garland, Progress in Coordination Chemistry, M. Cais Ed., Proc. 11th ICCC, Haifa and Jerusalem, 1968, p. 599.

Weiss law $\chi_p \propto \frac{1}{T+\Theta}$ where Θ is the Weiss constant, or more approximately by the Curie law $\chi_p \propto \frac{1}{T}$. The value of Θ is expected to be of the order of a few °K [2], so that the resulting magnetic moment $\mu_{eff} \propto \left[\frac{T}{T+\Theta}\right]^{1/2}$ should be fairly constant in the temperature range of interest (80-400°K).

Diamagnetism. Diamagnetic corrections, χ_D (per mole), were estimated from tabulated values.[35-37] Literature values of χ_D obtained by direct measurements are available for some ligands,[35] but where the ligands have been measured as solids, diamagnetic anisotropy is expected to give rise to some inaccuracy. Such inaccuracy could normally be disregarded, but in low spin d^6 complexes, χ_D is likely to be greater than χ^* so that it is better to calculate χ_D directly, or to use χ^D values obtained from measurements on liquids. Thus $\chi_D(\text{dipy}) = 2\chi^D(\text{py}) - 2\chi^D(\text{H})$, where dipy = 2,2'-dipyridyl and py = pyridine. $10^6\chi^D(\text{py}) = -49.21$ c.g.s.u.,[37] so that $10^6\chi^D(\text{dipy}) = -93$ c.g.s.u.

Experimental Section

The previously known complexes were prepared according to the standard methods.[3,38-40] A second sample of each of Fe(phen)$_3$(ClO$_4$)$_2$ and Fe(PAQHY)$_2$(ClO$_4$)$_2$ (PAQHY = 1-(2'-pyridyl)-3-(2''-quinolyl)-1,2-diaza-2-propene) was prepared by two recrystallisations from aqueous ethanol.

Fe(PAQHY)$_2$(ClO$_4$)$_2$. H_2O[3]. Calcd. for $C_{30}H_{26}N_8O_9Cl_2Fe$: C, 46.8; H, 3.4; Fe, 7.3. Found: C, 47.0; H, 3.5; Fe, 7.4. Fe(MPAPHY)$_2$(ClO$_4$)$_2$. H_2O[3] (MPAPHY = 1-(2'-pyridyl)-3-(6''-methyl-2''-pyridyl)-1,2-diaza-2-propene). Calcd. for $C_{24}H_{24}N_8O_9Cl_2Fe$: C, 41.3; H, 3.8; Fe, 8.0. Found: C, 41.7; H, 4.0; Fe, 8.1. Fe(PAQY)$_2$[3] (PAQY is the deprotonated form of PAQHY). Calcd. for $C_{30}H_{22}N_8Fe$: C, 65.5; H, 4.0; Fe, 10.2. Found: C, 65.2; H, 4.2; Fe, 9.9.

Fe(GMI)$_3$I$_2$ [39] Calcd. for $C_{12}H_{24}N_6I_2Fe$: C, 25.6; H, 4.3; Fe, 9.9. Found: C, 25.5; H, 4.5; Fe, 9.7. Fe(BMI)$_3$I$_2$.[39] Calcd. for $C_{18}H_{36}N_6I_2Fe$: C, 33.5; H, 5.6; Fe, 8.6. Found: C, 33.4; H, 5.9; Fe, 8.5. Fe(BBI)$_3$(BF$_4$)$_2$.[40] Calcd. for $C_{36}H_{22}N_6F_8B_2Fe$: C, 52.8; H, 8.9; Fe, 6.8. Found: C, 52.3; H, 9.2; Fe, 6.7.

Fe(dipy)$_3$(ClO$_4$)$_2$. 3H_2O. A.R. ferrous ammonium sulphate hexahydrate (0.5 g) was dissolved in nitrogen-saturated distilled water (100 ml) and dipy (0.6 g) added. Ethanol (20-30 ml) was then added and the solution stirred on a steam bath until the ligands dissolved. The solution was filtered and a slight excess of sodium perchlorate mixed into the filtrate. The mixture was allowed to stand until cool, then the red product was filtered off. Calcd. for $C_{30}H_{30}N_6O_{11}Cl_2Fe$: C, 46.3; H, 3.9; Fe, 7.2. Found: C, 46.0; H, 4.0; Fe, 7.2.

Fe(phen)$_3$(ClO$_4$)$_2$. 3H_2O. Similar to above preparation, using phen (0.76 g). Calcd. for $C_{36}H_{30}N_6O_{11}Cl_2Fe$: 50.9; H, 3.6. Found: C, 50.8; H, 3.5.

Fe(5-chlorophen)$_3$(ClO$_4$)$_2$. 2H_2O. Similar to above preparation, using 5-chloro-1,10-phenanthroline (5-chlorophen) (0.82 g). Calcd. for $C_{36}H_{35}N_6O_{10}Cl_2Fe$: C, 46.3; H, 2.7; N, 9.0; Fe, 6.0. Found: C, 46.2; H, 3.1; N, 8.9; Fe, 5.9.

Fe(dmdipy)$_3$(ClO$_4$)$_2$. 2H_2O. Similar to above preparation, using 4,4'-dimethyl-2,2'-dipyridyl (dmdipy) (0.71 g). Calcd. for $C_{36}H_{40}N_6O_{10}Cl_2Fe$: C, 51.3; H, 4 8; N, 10.0; Fe, 6.5. Found: C, 51.4; H, 4.7; N, 9.6; Fe, 6.4.

Fe(tmphen)$_3$(ClO$_4$)$_2$. 2H_2O. Similar to above preparation, using 3,4,7,8-tetramethyl-1,10-phenanthroline(tmphen) (0.90 g). Calcd. for $C_{48}H_{52}N_6O_{10}Cl_2Fe$: C, 57.7; H, 5.2; N, 8.4; Fe, 5.6. Found: C, 57.9; H, 5.1; N, 8.1; Fe, 5.6.

Fe(tmphen)$_3$Cl$_2$. 4H_2O. Similar to above preparation, using excess lithium chloride instead of sodium perchlorate. Calcd. for $C_{48}H_{56}N_6O_4Cl_2Fe$: C, 63.5; H, 6.2; N, 9.3; Fe, 6.2. Found: C, 63.8; H, 6.4; N, 9.1; Fe, 6.1.

Fe(tmphen)$_3$(NCS)$_2$. 5H_2O. Similar to above preparation, using excess ammonium thiocyanate. Calcd. for $C_{50}H_{58}N_8O_5S_2Fe$: C, 61.8; H, 6.0; N, 11.5; Fe, 5.8. Found: C, 61.4; H, 6.3; N, 11.2; Fe, 5.8.

Fe(5-chlorophen)$_3$Cl$_2$. 4H_2O. Preparation similar to that of Fe(5-chlorophen)$_3$(ClO$_4$)$_2$. 2H_2O, using excess lithium chloride instead of sodium perchlorate. Calcd. for $C_{36}H_{29}N_6O_4Cl_5Fe$: C, 51.3; H, 3.5; N, 10.0, Fe, 6.6. Found: C, 51.4; H, 3.7; N, 9.6; Fe, 6.4.

Fe(5-chlorophen)$_3$(NCS)$_2$. 3H_2O. Similar to above preparation, using excess ammonium thiocyanate. Calcd. for $C_{38}H_{27}N_8O_3Cl_3S_2Fe$: C, 52.5; H, 3.1; N, 12.9; Fe, 6.4. Found: C, 52.6; H, 3.2; N, 12.6; Fe, 6.3.

Fe(dmdipy)$_3$(NCS)$_2$. 3 . 5H_2O. Preparation similar to that of Fe(dmdipy)$_3$(ClO$_4$)$_2$. 2H_2O, using excess ammonium thiocyanate. Calcd. for $C_{38}H_{43}N_8O_{3\,.\,5}S_2Fe$: C, 57.9; H, 5.5; N, 14.2; Fe, 7.1. Found: C, 57.8; H, 5.5; N, 14.0; Fe, 7.1.

Fe(dmdipy)$_3$(NCSe)$_2$. 3$H_2$0. Similar to above preparation, using excess potassium selenocyanate. Calcd. for $C_{38}H_{42}N_8O_3Se_2Fe$: C, 52.3; H, 4.9; N, 12.8; Fe, 6.4 Found: C, 52.6: H, 4.8; N, 12.4; Fe, 6.4.

The magnetic measurements were made by the Gouy method.[41,42] The accuracy is about 2% for normal paramagnetic substances, but becomes poorer where the magnetism is weak, and the error may be as high as 20% for cases where diamagnetism makes the biggest contribution.

Results and Discussion

The magnetic susceptibilities of the complexes corrected for diamagnetism, χ^D, are listed in Table I. It

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(35) B. N. Figgis and J. Lewis, Ch. 6 of « Modern Coordination Chemistry ». Ed. J. Lewis and R. G. Wilkins, Interscience Publishers Inc., New York, 1960.

(36) P. W. Selwood, « Magnetochemistry ». Interscience Publishers, Inc., New York, 2nd Edition, 1956.

(37) Handbook of Chemistry and Physics Ed. C. D. Hodgman, Chemical Rubber Publishing Co., Cleveland. Ohio, 44th Edition, 1963, p. 2745.

(38) F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).

(39) P. Krumholz, *J. Amer. Chem. Soc.*, *75*, 2163 (1953).

(40) S. Otsuka, T. Yoshida and A. Nakamura, *Inorg. Chem.*, 6, 20 (1967).

(41) S. J. Gruber, C. M. Harris and E. Sinn, *J. Inorg. Nucl. Chem.*, *30*, 1805 (1968).

(42) C. M. Harris, H. R. H. Patil, and E. Sinn, *Inorg. Chem.*, 6, 1102 (1967).

is evident that in cases where magnetism is anomalously high (μ_{eff} is significantly higher than 1 B.M.), the susceptibility decreases rapidly with increasing temperature, suggesting that the magnetism arises mainly from paramagnetic impurities. This is confirmed by the fact that the paramagnetism of each of Fe(phen)$_3$(ClO$_4$)$_2$ and Fe(PAQHY)$_2$(ClO$_4$)$_2$ decreases upon recrystallisation, and the paramagnetism of Fe(MPAPHY)$_2$(ClO$_4$)$_2$ and Fe(PAQY)$_2$ varies from sample to sample. The literature μ_{eff} values of 1.9 and 1.8 B.M. for Fe(MPAPHY)$_2$(ClO$_4$)$_2$ and Fe(PAQY)$_2$ respectively suggest the possibility of a high spin - low spin crossover situation, but the results in Table 1 lead to uncorrected room temperature values of 1.2 and 1.4 B.M. respectively.

Since contribution of paramagnetic impurities χ_P is often much larger than χ^*, accurate χ^* values cannot be expected from the experimental data. For complexes in which E_1 is known, χ^* has been estimated from (3) and (4) using $k \doteqdot 0.7$. Then for the GMI, BMI and BBI complexes, the $10^6\chi^*$ value is about 100 c.g.s.u., and for $Fe(CN)_6^{4-}$ ($E_1 \doteqdot 31{,}000\ cm^{-1}$ [28]) and $Fe(phen)_3^{2+}$ ($E_1 \doteqdot 12{,}300\ cm^{-1}$ [28]) it is 80 and 200 respectively. For the other complexes $10^6\chi^*$ was taken as 200 c.g.s.u. Where χ_P ($=\chi_{obsd}-\chi^*$) is appreciably greater than the experimental greater than the experimental scatter, the χ_P values were fitted to a Curie-Weiss law of the form $\chi_P \propto 1/(T+\Theta)$ and the mean value of the magnetic moments due to paramagnetic impurities, corrected for the Weiss constant Θ were obtained from the relation

$$\mu_p = \frac{1}{n}\sum_{i=1}^{n} \sqrt{\{8.00\chi_p(i)[T(i)+\Phi]\}} \tag{11}$$

where n is the number of determinations of the susceptibility $\chi_p(i)$ at temperatures T(i). These values are listed in Table II. In each case where μ_p is no negligible, the Θ values are fairly small, indicating that impurities are normal paramagnetics.

Table I. Observed Magnetic Susceptibilities, χ_M, in c.g.s.e.m.u.

Fe(PAQHY)$_2$(ClO$_4$)$_2$ first sample											
T(°K)	89.0	117.2	165.3	218.7	292.0						
$10^6\chi_M$	1840	1432	1095	921	729						
Fe(PAQHY)$_2$(ClO$_4$)$_2$ second sample											
T(°K)	92.0	116.0	146.2	189.0	261.2	297.5	348.5				
$10^6\chi_M$	865	718	715	689	742	714	797				
Fe(PAQY)$_2$											
T(°K)	93.1	117.4	158.2	187.2	246.1	295.0	321.6	368.0			
$10^6\chi_M$	990	791	663	566	616	673	789	762			
Fe(MPAPHY)$_2$(ClO$_4$)$_2$											
T(°K)	84.2	100.4	127.2	148.9	178.2	209.6	252.0	292.2	343.0		
$16^6\chi_M$	1680	1510	1221	1030	949	873	844	839	762		
Fe(phen)$_3$(ClO)$_4$)$_2$. 3H$_2$O first sample											
T(°K)	97.5	138.2	162.0	231.4	297.2	345.0					
$10^6\chi_M$	1630	1225	1039	817	667	625					
Fe(phen)$_3$(ClO$_4$)$_2$. 3H$_2$O first sample											
T(°K)	93.6	114.8	150.6	181.5	223.4	242.1	276.1	276.2	308.0	320.5	364.0
$10^6\chi_M$	217	181	151	187	139	175	177	202	149	161	
Fe(dipy)$_3$(ClO$_4$)$_2$. 3H$_2$O											
T(°K)	108.1	145.6	190.0	243.1	297.6	335.0					
$10^6\chi_M$	324	286	204	265	280	234					
Fe(5-chlorophen)$_3$(ClO$_4$)$_2$. 2H$_2$O											
T(°K)	88.4	133.9	155.2	223.4	298.1	338.0					
$10^6\chi_M$	998	752	652	517	408	398					
Fe(tmphn)$_3$(ClO$_4$)$_2$. 2H$_2$O											
T(°K)	96.0	137.2	169.5	218.2	267.5	298.3	352.0				
$10^6\chi_M$	430	376	298	311	320	275	321				
Fe(tmphen)$_3$Cl$_2$. 4H$_2$O											
T(°K)	98.7	149.3	236.2	305.1							
$10^6\chi_M$	988	719	592	485							
Fe(tmphen)$_3$(NCS)$_2$. 5H$_2$O'											
T(°K)	87.4	100.4	114.8	148.1	179.1	223.4	293.2	319.2			
$10^6\chi_M$	323	195	164	250	274	257	158	181			
Fe(5-chlorophen)$_3$(NCS)$_2$. 5H$_2$O											
T(°K)	85.9	109.8	132.6	166.1	215.4	260.6	298.5	331.5			
$10^6\chi_M$	412	347	273	298	313	290	263	260			
Fe(5-chlorophen)$_3$(NCS)$_2$. 3H$_2$O											
T(°K)	86.4	104.9	141.5	179.6	212.4	242.9	268.8	303.0	329.0		
$10^6\chi_M$	2009	1866	1401	1197	1065	986	896	778	755		
Fe(dmdipy)$_3$(NCS)$_2$. 3 . 5H$_2$O											
T(°K)	85.2	123.2	159.5	196.0	229.5	257.4	294.5	327.0			
$10^6\chi_M$	2208	1632	1268	1110	988	949	738	732			
Fe(dmdipy)$_3$(NCSe)$_2$. 3H$_2$O											
T(°K)	87.2	114.7	139.5	174.2	208.1	239.4	266.1	299.0	332.2		
$10^6\chi_M$	568	548	410	340	284	254	252	237	261		
Fe(GMI)$_3$I$_2$											
T(°K)	95.2	128.5	163.0	212.3	282.8	324.5					
$10^6\chi_M$	320	210	186	142	138	110					
Fe(BMI)$_3$I$_2$											
T(°K)	92.0	134.6	158.0	203.4	251.0	295.2	324.0				
$10^6\chi_M$	425	351	290	280	235	188	190				
Fe(BBI)$_3$(BF$_4$)$_2$											
T(°K)	88.6	141.0	208.2	291.0	318.7						
$10^6\chi_M$	18020	1185	897	705	651						
K$_4$Fe(CN)$_6$											
T(°K)	96.2	137.1	195.0	253.2	298.0	352.1					
$10^6\chi_M$	250	139	153	56	98	80					

Table II. Mean magnetic moment contributions from paramagnetic impurities, μ_p, correctd for the Weiss constant Θ (equation (11)).

Compound	μ_p (B.M.)	Θ (°)
Fe(phen)$_3$(ClO$_4$)$_2$. 3H$_2$O[a]	1.08	6
Fe(5-chlorophen)$_3$(ClO$_4$)$_2$. 2H$_2$O	0.7	–18
Fe(tmphen)$_3$Cl$_2$. 4H$_2$O	0.85	21
Fe(5-chlorophen)$_3$(NCS)$_2$. 3H$_2$O	1.22	10
Fe(dmdipy)$_3$(NCS)$_2$. 3H$_2$O	1.15	–10
Fe(BBI)$_3$(BF$_4$)$_2$	1.20	16

The PAQHY, PAQY and MPAPY compplexes to be exceptional in that after correction of χ_{obsd} for $10^6\chi^* = 200$ c.g.s.u. and for a constant μ_p, estimated from.(11) with $\Theta = 0$, there remains a very small susceptibility (Table III), which might be the result of a very small thermal population of the $^5T_2$ state.[12] This susceptibility is too small to permit accurate estimates of the crossover parameters but corresponds to a separation at least as high as 3000 cm^{-1} between the $^1A_1$ and $^5T_2$ states. This contribution would be small for all temperatures at which the complexes are thermally stable. It is quite likely that this residual susceptibility, which is small compared to the sum of the other contributions, χ_D, χ_P and χ^*(results from experimental error, or a slight temperature dependence in χ_P. The absence of a significant degree of high spin low spin crossover behaviour in Fe(PAQHY)$_2$(ClO$_4$)$_2$ suggests that all the iron(II) complexes of PAPHY type[3] are essentially low spin over the accessible temperature range, and the anomalous moments result largely from paramagnetic impurities. In complexes with PAPHY ligands (LH) the iron(III) complex Fe(LH)(L)(ClO$_4$)$_2$, containing one deprotonated PAPY ligand (L) is analytically indistinguishable from the normal low spin iron(II) complex Fe(LH)$_2$(ClO$_4$)$_2$, and is a likely source of paramagnetic impurities. Such deprotonation with simultaneous oxidation of the central metal has been observed in some cases.[43]

(43) B. Chiswell, J. P. Geldard, A. T. Phillip and F. Lions, *Inorg. Chem.*, 3, 1272 (1964).

Table III. Magnetic Susceptibilities χ_{corr} of $Fe(PAQHY)_2(ClO_4)_2$, $Fe(PAQY)_2$, and $Fe(MPAPHY)_2(ClO_4)_2$ after correction for χ and χ_p.

$Fe(PAQHY)_2(ClO_4)_2$		$\mu_p = 0.70$ B.M.			
T(°K)	146.2	189.0	261.2	297.5	348.6
χ_{corr}	97	165	320	308	421
$Fe(PAQY)_2$	$\mu_p = 0.75$ B.M.				
T(°K)	246.1	295.0	321.6	368.0	
χ_{corr}	126	181	367	368	
$Fe(MPAPHY)_2(ClO_4)_2$		$\mu_p = 1.0$ B.M.			
T(°K)	178.2	209.6	252.0	292.2	343.0
χ_{corr}	37	68	141	205	192

The complexes with ring-substituted phenanthrolines and dipyridyls are all pure low spin, indicating either that $Fe(phen)_3(ClO_4)_2$ is further from the crossover than has previously been believed, or that the effect of the substituents is negligibly small. The substituents are not close enough to the coordinating nitrogens to exert any steric influence on the metal-ligand system, and they can affect Δ, and hence the magnetic properties, only through an electronic mechanism. The existence of such an electronic effect due to ring substituents in dipyridyls and phenanthrolines has been demonstrated in a series of bis(phen, dipy)-iron(II) complexes which are already in the crossover region and whose magnetic properties are therefore very sensitive to any perturbations in the environment of the central metal atom.[9,44] On the other hand, the effect of the steric crowding resulting from ring-substitution adiacent to the nitrogen atoms in bi- and tri-dentate ligands is found to be much more drastic, and can change a pure low spin (unsubstituted) iron(II) complex to pure high spin (substituted) together with a significant increase in metal-ligand bond length.[9,42,45] Although inaccuracy is introduced by the paramagnetic impurities, the temperature independent part of the paramagnetism, χ^*, in the present series of dipy and phen complexes appears to show significant variations according to the type of substitution, but more definite conclusions are best deferred at this stage, pending further corroborative evidence such as NMR data, and detailed electronic spectral assignments. However, it is apparent that none of the complexes have χ^* values above the estimated maximum of 300×10^{-6} c.g.s.u., and the results illustrate the utility of temperature dependent magnetic susceptibility measurements in evaluating the significance of anomalous room temperature magnetic moments.

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(44) E. Sinn, unpublished results.

(45) C. M. Harris, H. R. Patil, and E. Sinn, *Inorg. Chem. 8*, 101 (1969).