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SPIN TRANSITIONS IN SIX-COORDINATE IRON(II) COMPLEXES

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CONTENTS

LIGAND ABBREVIATIONS

bipy = 2,2′-bipyridine
5-Clbipy = 5-chloro-2,2′-bipyridine
2-Clphen = 2-chloro-1,10-phenanthroline
5-Clphen = 5-chloro-1,10-phenanthroline
dimebipy = 4,4′-dimethyl-2,2′-bipyridine
dimephen = 4,7-dimethyl-1,10-phenanthroline
$HB(dimepz)_3$ = hydro-tris(3,5-dimethyl-1-pyrazolyl)borate
$HB(pz)_3$ = hydro-tris(1-pyrazolyl)borate
mal = malonate
mephen = 2-methyl-1,10-phenanthroline
5-mephen = 5-methyl-1,10-phenanthroline
5-NO_2phen = 5-nitro-1,10-phenanthroline
ox = oxalate

paptH = 2-(2-pyridylamino)-4-(2-pyridyl)thiazole
papt = 2-(2-pyridylamino)-4-(2-pyridyl)thiazolate
pbbt = 2,2′-(pyridine-2,6-diyl)bisbenzothiazole
pbi = 2-(2-pyridyl)benzimidazole
pbuti = *N*-(1,10-phenanthrolin-2ylmethylene)*t*-butylamine
phen = 1,10-phenanthroline
5-phphen = 5-phenyl-1,10-phenanthroline
picam = 2-picolylamine
ppa = *N*′-(2-pyridylmethyl)picolinamidine
pphy = 1,10-phenanthroline-2-carbaldehyde phenylhydrazone
ppi = *N*-(2-pyridylmethylene)phenylamine
py = pyridine
pyi = 2-(2-pyridyl)imidazole
pyim = 2-(2-pyridyl)imidazoline
pythiaz = 2,4-bis(2-pyridyl)thiazole
terpy = 2,2′,2″-terpyridine
tetmephen = 3,4,7,8-tetramethyl-1,10-phenanthroline

A. INTRODUCTION

The compounds of iron(II), along with those of iron(III), have long provided the classic illustrations for the classification of six-coordinate metal complexes in terms of the number of unpaired electrons on the metal atom. Thus in the high-spin hexaaquo iron(II) ion and the low-spin hexacyanoferrate(II) ion there are 4 and 0 unpaired electrons, respectively, on the metal atom. The notion that these two species represent extreme situations and that there should exist a situation in which both electronic configurations are almost equally favourable was proposed by Pauling [1] and is certainly implicit in ligand-field theory. Inspection of the Tanabe—Sugano diagram for the d^6 configuration in an octahedral field shows that there is a value for the field strength [2] beyond which the ground state of the metal atom changes from $^5T_2$ to $^1A_1$. A "spin crossover" or "spin transition" can be expected to be induced when the field strength about the metal atom is in the vicinity of this critical value such that the application of relatively minor external perturbations, such as a variation in temperature, can tip the scales in favour of one or other of the ground states. Such spin transitions are feasible in the octahedral complexes of metal ions of configuration d^4, d^5, d^6 or d^7. The changes in spin associated with the configurational changes displayed by the d^8 ion, Ni^{2+}, in certain of its (distorted) six-coordinate complexes [3] differ only in degree rather than kind, since in all instances in which a change in the spin multiplicity occurs some concomitant rearrangement of the coordination geometry is to be expected.

Certainly the most extensively studied, but in some respects still the most enigmatic [4,5], of spin transitions in six-coordinate complexes is that which occurs in the tris(*N*,*N*-dialkyldithiocarbamato)iron(III) complexes. These systems, along with others known at the time, were reviewed comprehensively in 1968 by Martin and White [6] who also gave a thorough treatment of the theoretical and experimental variation in physical properties accompanying spin transitions. Since then aspects of spin transitions have been reviewed by several authors [3,7–13]. The present review is concerned only with those transitions which occur in six-coordinate iron(II) complexes, not because these are fundamentally any different from those which occur in other systems, but because, for iron(II), a sufficiently large number of examples has now been reported to enable the recognition of some general trends in the occurrence and manifestation of a spin transition.

B. IRON(II) CROSSOVER SYSTEMS

It might reasonably be expected that the critical conditions apparently necessary for the occurrence of nearly equi-energetic ground states would be met only rarely, and then perhaps by chance. The first report of the existence of a "spin equilibrium" in six-coordinate iron(II) would seem to be that by James et al. [14] who observed unexpectedly low but strongly temperature-dependent intensity in the visible spectrum of the tris(5,5′-diethylcarboxylate-2,2′-bipyridine)iron(II) ion. This complex was found also to have much lower stability than [Fe phen$_3$]$^{2+}$. It was concluded that the complex was not entirely low-spin but an equilibrium mixture of the two spin forms. Magnetic data were said to support this conclusion but the system has not been reported in detail. Spin transitions were first positively recognised in synthetic iron(II) systems only about ten years ago. Since the initial report [15] the number of such systems has increased rapidly and a significantly large proportion of these can be considered to be modifications of the low-spin [Fe phen$_3$]$^{2+}$, [Fe bipy$_3$]$^{2+}$ or [Fe terpy$_2$]$^{2+}$ species. It is worth recalling that as long ago as 1956 Orgel [16] suggested that the field strength of phenanthroline should lie near that at the iron(II) spin crossover. The perception of Orgel's early observations is well supported by the recent reports [17,18] of the pressure-induced spin transitions in salts of [Fe phen$_3$]$^{2+}$ and [Fe bipy$_3$]$^{2+}$. These particularly interesting transitions have been reviewed by Drickamer and Frank [19] and, though in principle not so different from the (usually) temperature-induced transitions considered in this review, are not discussed here further.

(i) Bis(phenanthroline) and related systems

The replacement of water molecules in [Fe(H$_2$O)$_6$]$^{2+}$ progressively by phenanthroline effects spin pairing in the metal atom only on coordination of the third molecule of the heterocyclic base [20], giving rise to the anomalous order for the values of the stepwise formation constants for [Fe phen$_3$]$^{2+}$. It has been known for some time that the spin-state of the metal atom in the bis(phenanthroline) complexes [Fe phen$_2$X$_2$] is dependent on the nature of

TABLE 1

Magnetic properties of [Fe phen_2X_2]

X	μ (B.M.)	T (K)	Ground state
I	5.13	294	$^5T_2$
I	5.11	111	$^5T_2$
Br	5.15	295	$^5T_2$
Br	5.23	111	$^5T_2$
Cl	5.27	291	$^5T_2$
Cl	5.28	111	$^5T_2$
N_3	5.14	295	$^5T_2$
N_3	5.15	110	$^5T_2$
NCO	5.10	294	$^5T_2$
NCO	4.97	91	$^5T_2$
HCOO	5.27	293	$^5T_2$
HCOO	5.36	91	$^5T_2$
NCS	5.17	293	$^5T_2$
NCS	0.65	77	$^1A_1$
NCSe	4.98	293	$^5T_2$
NCSe	0.84	77	$^1A_1$
CN	0.61	303	$^1A_1$
CNO	0.31	293	$^1A_1$
NO_2	0.98	293	$^1A_1$

Data taken from Refs. 8 and 24.

the X group. Thus [Fe $\text{phen}_2(\text{CN})_2$] is diamagnetic [21], whereas [Fe phen_2Cl_2] is paramagnetic [22] with a moment of 5.3 B.M. It would seem reasonable therefore to take as a likely system for observing a spin transition in iron(II) a complex [Fe phen_2X_2] in which X provides a field strength intermediate between that of the chloride ion and that of the cyanide ion. The systematic variation of X in [Fe phen_2X_2], in an attempt to define the crossover conditions for iron(II), was reported by Madeja and König in 1963 [23]. Although these workers had, at that stage, produced crossover systems ([Fe $\text{phen}_2(\text{NCS})_2$] and [Fe $\text{phen}_2(\text{NCSe})_2$]) they were not recognised as such since measurements were confined to room temperature. Shortly afterwards Baker and Bobonich [24] reported the anomalous temperature dependence of the magnetism of [Fe $\text{phen}_2(\text{NCS})_2$] and, though they considered the possibility that this might represent a spin transition, they rejected this interpretation, being guided by Mössbauer effect data [25] which were later shown to be in error. Infrared data reported by Baker and Long [26] were consistent with a change in ground state of the metal atom and this was later conclusively shown by the magnetic and Mössbauer effect data of König and Madeja [15]. Similar behaviour was later reported [27] for [Fe $\text{bipy}_2(\text{NCS})_2$]. The magnetic properties of [Fe phen_2X_2] are summarised in Table 1.

The temperature-dependence of the magnetism of [Fe $\text{phen}_2(\text{NCS})_2$], [Fe $\text{phen}_2(\text{NCSe})_2$] and [Fe $\text{bipy}_2(\text{NCS})_2$] is characterised by a precipitous decrease, within a few degrees, from a value typical for high-spin iron(II) to one more or less normal for the low-spin state (Fig. 1). Such an abrupt change in spin state is not typical of spin transitions and, although opinion initially differed on this point [28—30], is associated with a first order phase change in the solid. This has been conclusively demonstrated for [Fe phen$_2$(NCS)$_2$] and [Fe phen$_2$(NCSe)$_2$] by Sorai and Seki [31], who observed an anomaly in the heat capacity of these compounds at the spin transition temperature. The occurrence of a phase transition may well be associated with the changes in the intramolecular dimensions which are predicted to accompany a high-spin $\rightleftharpoons$ low-spin transition [32,33]. These changes have been confirmed directly by the determination of the structure of [Fe bipy$_2$(NCS)$_2$] at temperatures above and below the spin transition temperature [30]. Structural data for this complex, which has a *cis* configuration, are illustrated in Fig. 2. In the $^5T_2$ and $^1A_1$ states the mean Fe—N distances were found to be 2.14 and 2.02 Å, respectively. This difference in bond lengths corresponds to a difference in ligand field strength in the two spin states in good agreement with the difference obtained directly from the electronic spectra of the high-spin and low-spin forms of the corresponding phenanthroline complex, which can be expected to have an essentially similar structure [34].

The effects of substituents in the heterocyclic ring systems have been studied [35—37] in several complexes closely related to [Fe phen$_2$(NCS)$_2$] or [Fe bipy$_2$(NCS)$_2$]. The sharp transition observed in the parent complexes is reproduced in the complex of 4,7-dimethyl-1,10-phenanthroline and its α-picoline solvate, but in the complexes of 4-methyl, 4-chloro, 4-cyano, 4-carbethoxy, 5-chloro, 5-methyl, 5-phenyl and 5-nitro-1,10-phenanthroline and 4,4′-dimethyl-2,2′-bipyridine the transition from the $^5T_2$ to the $^1A_1$ state occurs over a much broader range of temperature. Somewhat unexpectedly, in the complexes [Fe dimephen$_2$(NCS)$_2$],2py and [Fe tetmephen$_2$(NCS)$_2$],H$_2$O no transition at all was observed at temperatures above 77 K. A transition may well occur at lower temperatures. Similarly in the complex [Fe mephen$_2$(NCS)$_2$] no spin

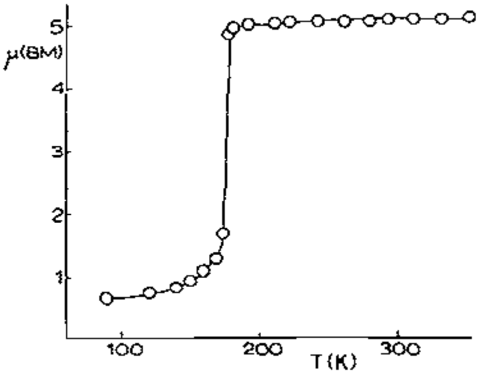


Fig. 1. Temperature dependence of the magnetic moment of [Fe phen$_2$(NCS)$_2$].

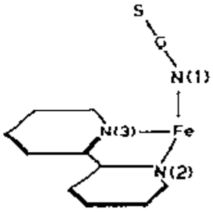


Fig. 2. Structural data for [Fe bipy$_2$(NCS)$_2$]. Bond lengths (a) 295 K: Fe—N(1) 2.09 Å; Fe—N(2) 2.17 Å; Fe—N(3) 2.17 Å; (b) 100 K: Fe—N(1) 2.01 Å; Fe—N(2) 2.05 Å; Fe—N(3) 2.01 Å.

transition was observed [38], but in this instance the substituent is adjacent to a donor atom and thus sterically prevents the close approach to the metal atom necessary for spin-pairing. Steric effects arising from coordination of the five-membered heterocycle in 2-(2-pyridyl)imidazole [39] and 2-(2-pyridyl)-benzimidazole [40] are probably also responsible for the purely high-spin nature of the complexes [Fe pyi$_2$(NCS)$_2$] and [Fe pbi$_2$(NCS)$_2$]. For the benzimidazole ligand the complex [Fe pbi$_2$(CN)$_2$] is also high-spin, at least at room temperature. Paramagnetism for this class of compound is unusual and its temperature dependence should be of interest.

Intermediate magnetic moments and Mössbauer spectra which show a single quadrupole doublet have been found [41,42] for certain of the complexes [FeL$_2$X$_2$] (L = phen, 2X = ox, mal; X = F; L = bipy; 2X = ox, mal; L = dimephen; 2X = ox, mal). For these a triplet ground state has been postulated although this interpretation has been questioned by Baker and Garland [43] who consider that the complexes represent mixtures of species with $S = 0$ and $S = 2$ ground states. The Tanabe—Sugano diagrams for the d^6 configuration show that in the neighbourhood of the $^5T_2 \rightleftharpoons {}^1A_1$ crossover the lowest-lying triplet state ($^3T_1$) reaches its lowest energy relative to that of the ground state. In a field of symmetry lower than O_h a triplet may in fact become the ground state because of splitting of the $^3T_1$ state [44]. The magnetism and Mössbauer effect have been investigated for certain of the above compounds at very low temperatures and the results have been interpreted in terms of a $^3A_2$ ground state in a (tetragonally) distorted field [45,46].

Complexes of formula [FeL$_2$(NCS)$_2$] . 2H$_2$O where L = phen, 5-Clphen, 5-phphen, 5-NO$_2$phen, 5-mephen, are also believed to have a triplet ground state [37]. Their magnetic moments are essentially temperature independent and fall in the range 2.85 ± 0.5 B.M. In these instances the presence of the water molecules appears to play a decisive role; the corresponding compounds formulated as monohydrates all undergo a $^5T_2 \rightleftharpoons {}^1A_1$ spin transition. It has been proposed that the complex [Fe dimephen$_2$(NCS)$_2$] can exist in either a quintet or a triplet form [47].

Finally, the co-existence of quintet and singlet forms of [Fe bipy$_2$(NCS)$_2$] as separate and non-interconvertible chemical entities within the one crystal lattice [48] completes the rich variety of behaviour displayed by these bis(diimine) chelates.

The magnetism of the complex [Fe phen $py_2(NCS)_2$], which must be closely related structurally to [Fe $phen_2(NCS)_2$], changes abruptly in the range 180—185 K due to a quintet—singlet transition [49]. Despite the lower position of pyridine in the spectrochemical series, the electronic spectra reveal that the average field strength in the mono(phenanthroline) complex (Δ = 11700 cm^{-1}) is only 200 cm^{-1} less than that in the bis(phenanthroline) complex [50].

A gradual decrease in the magnetic moment of dithiocyanato bis(*N*-phenyl-2-pyridinaldimine)iron(II) from 4.50 B.M. at 293 K to 3.30 B.M. at 80 K (and below) was interpreted in terms of a quintet ($^5T_2$)—triplet ($^3T_1$) transition [51] but Mössbauer spectra show two quadrupole-split doublets with parameters typical for singlet ($^1A_1$) and quintet ($^5T_2$) iron(II) and thus the change in magnetism was ascribed to a $^5T_2 \rightleftharpoons {}^1A_1$ transition, with a large residual $^5T_2$ fraction [52].

(ii) Bis(2-substituted-phenanthroline) derivatives

Incorporation of a donor-atom-containing substituent into the 2-position of phenanthroline produces a tridentate chelating agent (phen-2-X). Because of the rigid nature of the phenanthroline moiety the tridentate molecules must remain essentially planar thereby bringing the X groups into *cis* positions about the metal atom in [Fe(phen-2-X)$_2$], as they are in [Fe $phen_2X_2$]. Thus the two kinds of complex are chemically and structurally very closely related. Variation of the group X in the tridentate derivatives may be expected to have a similar effect on the ground state of the metal atom as the changes in X in [Fe $phen_2X_2$]. The available data are summarised in Table 2. The most striking effect is observed by replacement of the carboxamido by the carbothioamido group whereby the ground state changes from $^5T_2$ to $^1A_1$. The former group is believed to be O-bonded and the latter S-bonded. This effect of replacement of an O- by an S-donor finds a precedent [59] in the existence of high-spin, O-bonded and low-spin, S-bonded forms of bis(*p*-toluenesulphinato)bis(bipyridine)iron(II).

(iii) Tris(2-methyl-phenanthroline) and related systems

The importance of steric effects in determining the ground state of iron(II) in complexes containing imine-type bidentate chelate groups was shown by Robinson and Busch [60] for the complexes of 2-pyridinalmethylhydrazone and 2-pyridinaldimethylhydrazone which are low-spin and high-spin, respectively. The paramagnetism and relatively low stability of the tris(2-methyl-phenanthroline)iron(II) ion has been ascribed to the effect of the 2-methyl group in hindering the close approach of the ligand to the metal atom [61]. In contrast to the unsubstituted system, the stepwise formation constants for

TABLE 2

Magnetic properties of $[Fe(phen\text{-}2\text{-}X)_2]$

Complex	μ (B.M.)	T (K)	Ground state	Ref.
$[Fe(phen\text{-}2\text{-}COO)_2]$	5.19	298	$^5T_2$	53
	5.05	118	$^5T_2$	53
$[Fe(phen\text{-}2\text{-}CONH_2)_2][ClO_4]_2$	5.3	303	$^5T_2$	54, 55
	4.9	83	$^5T_2$	54
$[Fe(phen\text{-}2\text{-}CSNH_2)_2][ClO_4]_2$	0.7	295	$^1A_1$	56
$[Fe(phen\text{-}2\text{-}CSNH)_2]$	0.9	295	$^1A_1$	56
$[Fe(phen\text{-}2\text{-}CSNHC_6H_5)_2][BF_4]_2$	0.8	303	$^1A_1$	57
$[Fe(phen\text{-}2\text{-}CSNC_6H_5)_2]$	0.9	303	$^1A_1$	57
$[Fe(phen\text{-}2\text{-}C(=NOH)NH_2)_2][ClO_4]_2$	0	298	$^1A_1$	58

$[Fe\ mephen_3]^{2+}$ follow the normal order ($\log k_1 = 4.2$; $\log k_2 = 3.7$; $\log k_3 = 2.9$). The magnetic moments of salts of this complex cation are strongly temperature dependent, due to a gradual transition from the $^5T_2$ to the $^1A_1$ state at low temperatures [62]. The minimum in the χ'_M vs T curve and the levelling off of the magnetic moment to a value well in excess of that expected for low-spin iron(II), evident in Fig. 3, indicate that the transition does not proceed to completion. Mössbauer effect measurements confirm that for these salts there is a high fraction of molecules which remain in the $^5T_2$ state at cryogenic temperatures and is principally responsible for this residual paramagnetism [63, 64]. The fraction varies from one salt to another. Retention of a fraction of "permanently high-spin" species is a general phenomenon associated with $^5T_2 \rightleftharpoons {}^1A_1$ transitions in iron(II) and is considered further in Section C(ii).

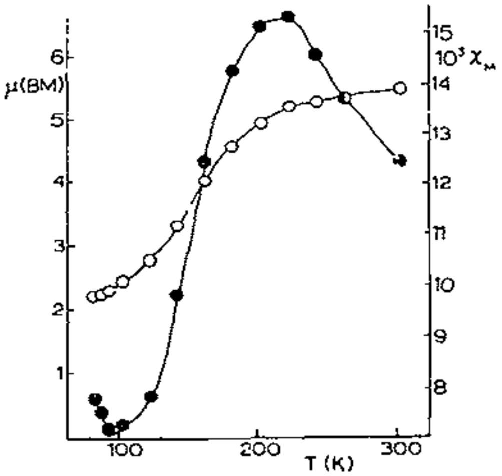


Fig. 3. Temperature dependence of the magnetism of $[Fe\ mephen_3][BPh_4]_2$.

A recent report [65] indicates that in tris(2-methoxy-phenanthroline)-iron(II) perchlorate a $^5T_2 \rightleftharpoons {}^1A_1$ transition occurs. In contrast to the [Fe me-phen$_3$]$^{2+}$ systems, the transition to low-spin is apparently almost complete and occurs at somewhat higher temperature, possibly due to the differences in the steric and electronic properties of the methyl and methoxy groups. A small, but significant, temperature dependence of the magnetic moment of tris(2-pyridinal-*o*-methylphenylimine)iron(II) perchlorate, which contains a substituted di-imine ligand sterically related to 2-methylphenanthroline, was ascribed to a transition from a singlet to a state of "higher spin multiplicity" [51]. Mössbauer effect results for this complex have been inconclusive although they do reveal that a singlet—quintet transition is definitely not involved [52]. On the basis of the observation of a relatively small decrease in magnetic moment over an extended temperature range it was suggested that both tris(2-chloro-phenanthroline)iron(II) perchlorate [55] and the corresponding complex of 2-(2-pyridyl)quinoline [66] are crossover systems. Steric effects of the substituents in these ligands might be expected to be similar to those of the methyl group in 2-methyl-phenanthroline but, at least for [Fe2-Clphen$_3$][ClO$_4$]$_2$, a spin transition does not occur since only a single doublet is observed in the Mössbauer spectrum at 4.2 K and this has parameters typical for the quintet state [67]. Reiff and Long suggest that the temperature dependence of the magnetic moment may be interpreted in terms of the influence of a low symmetry component to the ligand field together with spin—orbit coupling and covalency effects.

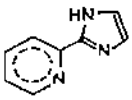
Substitution of phenanthroline at positions other than those adjacent to the donor atoms does not affect the field strength markedly and the tris(ligand) iron(II) complexes are low-spin [68].

(iv) Tris complexes of di-imines containing a five-membered heterocycle

The field strength of phenanthroline may be effectively reduced by replacement of one of the heterocyclic rings with a five-membered ring. Thus it has been reported [69] that pyrido-(2,3)-benzothiazole (I) coordinates poorly to

(I)

iron(II) and only bis complexes could be isolated. Such modifications of the phenanthroline structure are difficult to achieve synthetically, but for the completely analogous (at least in this context) bipyridine system are relatively simple and are generally effected by building up a five-membered heterocycle on to the 2-position of pyridine. Because of the relatively unfavourable (for coordination) position of the hetero atom of the five-membered ring the field strength of the resulting bidentate can be expected to be lower than that of the parent base. Several bidentates of this class (II—V) have been shown to induce a $^5T_2 \rightleftharpoons {}^1A_1$ transition in iron(II). The anomalous magnetic properties of the tris(2-(2-pyridyl)imidazole)iron(II) ion were reported almost simultaneously by Goodgame and Machado [70] and by Dosser et al. [71]. The deep red [Fe pyi$_3$][ClO$_4$]$_2$. H$_2$O was originally reported [72] to have a magnetic moment of 5.42 B.M. at 293 K. Goodgame and Machado found a value of 2.50 B.M. at the same temperature and showed that the moment was strongly temperature dependent arising from a $^5T_2 \rightleftharpoons {}^1A_1$ transition. Essentially similar results were later reported by Sasaki and Shigematsu [73]. Dosser et al. [71] investigated a series of salts of [Fe pyi$_3$]$^{2+}$, including a perchlorate dihydrate for which the moment decreased from 2.78 B.M. at 293.3 K to 0.94 B.M. at 93.3 K. The other salts investigated showed similar or even greater temperature dependence of the moments. Tris(2-(2-pyridyl)imidazoline)iron(II) perchlorate displays an interesting instance of magnetic isomerism. A dark blue low-spin form was isolated from ethanol and a dark purple form from propan-2-ol. The latter form has a moment of 5.25 B.M. at 295 K but this drops abruptly at about 120 K and is 2.7 B.M. at 83 K. It was suggested that the difference in properties of the two forms may be due to vicinal and meridional isomers, possible because of the unsymmetrical nature of the bidentate group [74]. The total field strength in such isomeric forms would not need to be greatly different to lead to the observed behaviour. More subtle variations in the structure or differences in the packing arrangements in the crystals could also be responsible for the differences. The two forms show different X-ray powder patterns and a complete structure analysis should be revealing. The differences in the reported magnetic properties of [Fe pyi$_3$][ClO$_4$]$_2$. H$_2$O appear also to indicate magnetic isomerism which may result from similar effects. The corresponding complex of 2-(6-methyl-2-pyridyl)imidazole remains high-spin, at least to 77 K, the additional steric effect of the methyl group rendering coordination less favourable [73].



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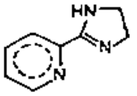

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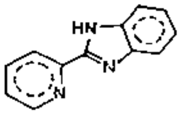

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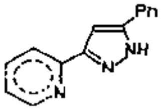

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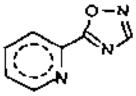
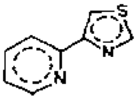


(VI)

The complex cation derived from 2-(2-pyridyl)benzimidazole (IV) has been studied by several groups. Sams et al. [75] reported the properties of the bromide, the nitrate monohydrate and the perchlorate dihydrate, for all of which temperature dependence of the magnetic moment was observed, that of the perchlorate being most pronounced and corresponding to an almost complete transition from the high-spin state at 300 K to the low-spin at 80 K. Sasaki and Shigematsu [73] reported data for a complex perchlorate monohydrate which differ somewhat, the moment at 77.2 K being 3.33 B.M. Machado [11] discussed the properties of a form of the perchlorate "prepared from acetone" which seem to be similar to those of the monohydrate described by Sams et al.

Solution studies indicate that 4-(2-pyridyl)thiazole (VII) coordinates more strongly to iron(II) than does (II) but less strongly than bipyridine [76]. Solid tris(ligand) complexes do not seem to have been isolated but their magnetism would be of interest. Lindoy and Livingstone reported [77] that attempts to isolate such salts of the related 2-(2-pyridyl)benzothiazole were unsuccessful.

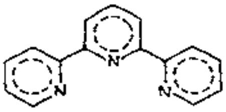


(VII)

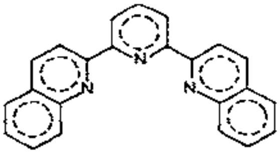
The tris(ligand) iron(II) complex perchlorate of 3-phenyl-5-pyridyl-2-(2)-pyrazole (V) has a magnetic moment which varies gradually from about 4.5 B.M. at 290 K to 2.9 B.M. at 110 K and this change has been ascribed to a $^5T_2 \rightleftharpoons {}^1A_1$ transition [78]. Similar behaviour has been observed [79] for the corresponding complex fluoroborate of the oxadiazole (VI).

(v) Bis(ter-imine) systems

2,2',2"-Terpyridine (VIII) can be considered the model ter-imine chelate group and effects spin-pairing [80] in iron(II) and a spin transition [81] in cobalt(II). Modifications of the structure of this model may be made so as to reduce the field strength to an extent that a change in ground state for iron(II) may occur. Thus Harris et al. [82] have shown that 2,6-di(2-quinolyl)pyridine (IX) yields a bis-ligand iron(II) complex which remains high spin over the range 85—341 K, the steric crowding due to the hydrogen atoms in the 8-position of the quinoline rings apparently preventing the necessary close approach of the donor atoms to the metal atom in the $^1A_1$ state. It is suggested that steric effects are also responsible for the different ground states of iron in the complexes of di-(2-pyridylmethyl)amine (X) and its N-methyl derivative [83].

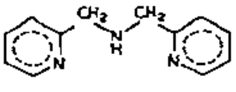


(VIII)



(IX)

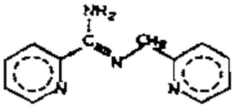
The tridentate (X) does not belong to the ter-imine class but can be considered as an intermediate between the completely aliphatic polyamines and the



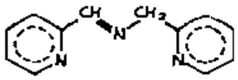
(X)

ter-imines such as terpyridine. In the bidentate series 2-picolylamine occupies a similar position with respect to bipyridine and ethylenediamine and indeed salts of its tris(ligand) iron(II) complex undergo a temperature-induced spin transition [84].

N'-(2-pyridylmethyl)picolinamidine (XI) is structurally related to terpyrid-



(XI)



(XII)

ine and other ter-imine systems such as (XII) which give low-spin iron(II) derivatives [85]. Although salts of the iron(II) complex of (XI) have low magnetic moments at room temperature, at elevated temperatures they become strongly paramagnetic, indicative of a change in spin-state [86]. The ability of the amidine (XI) to effect a spin transition in iron(II) presumably results from a reduction in field strength caused by the uncoordinated amino group and suggests that certain other tridentates of this class, in particular pyridine-2-aldehyde-2-pyridylhydrazone and its derivatives [87], may have field strengths near that at the iron(II) crossover, though studies of the temperature dependence of the magnetism of their iron complexes do not reveal this [88]. The introduction of methyl substituents into positions adjacent to the pyridine nitrogen atoms in (XI) results in the formation of a completely high-spin iron complex.

From 1,10-phenanthroline-2-carbaldehyde a series of ter-imine type ligands has been obtained by condensation with primary amines. In this way the effects of the introduction of substituents adjacent to one of the donor atoms have been studied for the imine [89] and hydrazone [90] derivatives listed in Tables 3 and 4. In these instances both steric and electronic effects of the substituent groups are presumably operative but the steric appear to predominate. Thus for the hydrazones a range of magnetic behaviour was encountered in the iron complexes. Those containing relatively small substituents give rise to low-spin complexes, the phenylhydrazone yields a complex which shows a sharp spin transition and the complex of the pyridylhydrazone is essentially high-spin within the range 83—303 K. Again in the imine series steric factors exert a strong influence on the ground state of the metal atom. That containing the bulky tertiary butyl group induces a $^5T_2 \rightleftharpoons {}^1A_1$ transition but the remainder favour spin-pairing. It is noteworthy that for the same series of imines $^4T_1 \rightleftharpoons {}^2E$

TABLE 3

Magnetic properties of $[FeL_2][BF_4]_2$

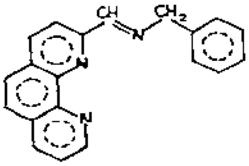
L =

R	μ (303 K)	μ (83 K)
CH_3	0.7	0.6
$CH(CH_3)_2$	1.0	0.8
CH_2CH_3	1.0	0.6
$(CH_2)_2CH_3$	0.9	0.8
$(CH_2)_3CH_3$	1.6	1.0
$CH(CH_3)CH_2CH_3$	1.5	1.0
$C(CH_3)_3$	4.9	2.0
C_6H_5	1.2	0.6
$CH_2C_6H_5$	1.0	0.9

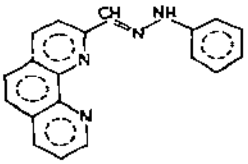
Data taken from Ref. 89.

transitions can be induced in cobalt(II), but only by those ligands which produce iron(II) complexes with a $^1A_1$ ground state.

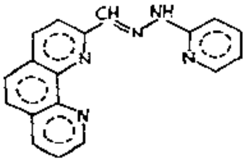
Comparison of the properties of the iron complexes of the three closely related ligands (XIII—XV) shows how sensitive these can be to seemingly minor structural changes when the ligand field strengths are in the crossover region.



(XIII)



(XIV)



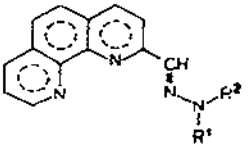
(XV)

Thus (XIII) effects spin-pairing, in the complex of (XIV) a spin transition occurs and (XV) yields a high-spin complex. The behaviour of (XV) is in contrast

TABLE 4

Magnetic properties of $[FeL_2][BF_4]_2$

L =



R^1	R^2	μ (303 K)	μ (83 K)
H	C_6H_5	5.3	0.6
H	CH_3	1.70	1.41
CH_3	CH_3	5.50	4.41
CH_3	C_6H_5	5.1	5.1
C_6H_5	C_6H_5	5.0	5.0
H	2-pyridyl	5.2	4.8

Data taken from Ref. 90.

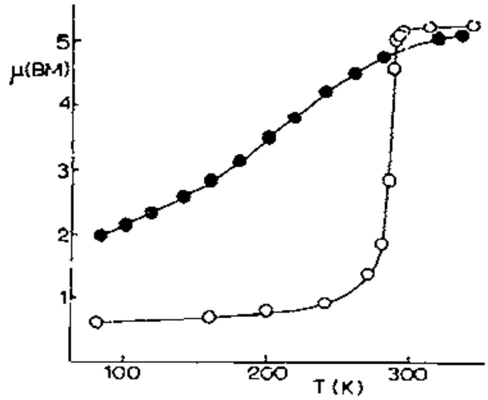
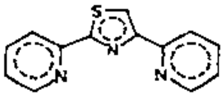


Fig. 4. Temperature dependence of the magnetic moment of [Fe pphy$_2$][BF$_4$]$_2$ (open circles) and [Fe pbuti$_2$][BF$_4$]$_2$ (closed circles).

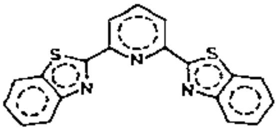
to that of its pyridine analogue which gives a low-spin iron(II) complex [91]. This difference arises from the steric barrier to coordination provided by the free pyridyl group in (XV).

Although both the phenylhydrazone and the *t*-butyl-imine derivatives effect an almost complete spin transition in iron(II) within the range 83—303 K, the nature of the transition is different in the two instances. Whereas the change in magnetic moment in the imine derivative is gradual, that in the hydrazone is abrupt and is virtually complete just below room temperature (Fig. 4).

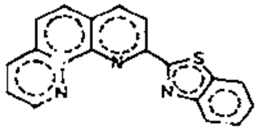
Modification of the terpyridine model by replacement of one (or more) of the pyridine rings by a five-membered heterocycle has been shown in several instances to have the same effect on the spin-state of iron as similar changes in the bipyridine system. Thiazole (XVI) [92—95], benzothiazole (XVII, XVIII) [95,96], thiazolidine (XIX) [95], oxadiazole (XX) [97], imidazoline (XXI) [98] and benzimidazole (XXII) [98] moieties have been incorporated into the terpyridine framework and in each instance a $^5T_2 \rightleftharpoons {}^1A_1$ transition appears to be induced in the iron(II) bis-ligand complex. The distortions already present in the complexes of terpyridine [99—102] will be magnified in those of



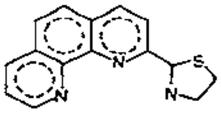
(XVI)



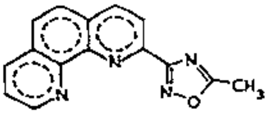
(XVII)



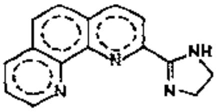
(XVIII)



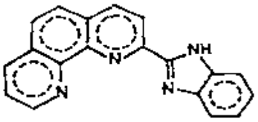
(XIX)



(XX)



(XXI)

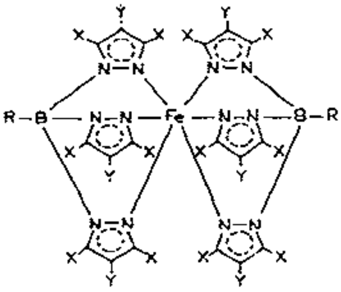


(XXII)

the tridentates containing a five-membered heterocycle, a factor probably of major consequence contributing to the ability of these ligands to bring about a spin transition.

(vi) Other systems

Spin transitions have been reported for several additional six-coordinate iron(II) systems which contain ligands which cannot be classified as di-imines or ter-imines. The bis(tris(1-pyrazolyl)borato)iron(II) complexes (XXIII) provide one of the best examples of a spin transition involving $S = 0$ and $S = 2$ states and constitute one of the few iron(II) crossover systems to have been studied in detail both in solution and in the solid state [103,104].

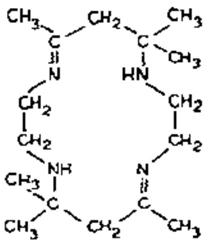


(XXIII)

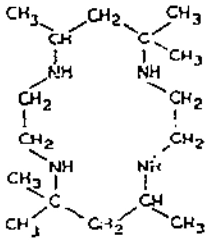
XXIIIa : R = 1-pyrazolyl, X = Y = H
XXIIIb : R = C_6H_5; X = Y = H
XXIIIc : R = H; X = Y = H
XXIIId : R = H; X = CH_3; Y = H
XXIIIe : R = H; X = Y = CH_3

The manifestation of a spin transition in these complexes is sensitive to both the nature of the ligand substituents and the physical state of the complex. Thus in solution (XXIIIa) and (XXIIIb) are low-spin, (XXIIIc) displays a spin transition and (XXIIId) and (XXIIIe) are high-spin. In the solid state (XXIIIe) remains high-spin over the temperature range 300—4.2 K. However, in the same range (XXIIId) undergoes an almost complete $^5T_2 \rightleftharpoons {}^1A_1$ transition and (XXIIIc) is entirely low-spin, although at temperatures above 300 K conversion to the high-spin form occurs and at 500 K the magenta colour due to the low-spin species has been lost. There is, then, in these complexes a favouring of the low-spin state in the solids, and it was suggested that this is due to an additional component to the crystal field arising from packing in the lattice.

Busch and co-workers [105,106] have studied the spin-state and stereochemistry of the iron(II) complexes of the macrocyclic quadridentates (XXIV) ([14]dieneN$_4$) and (XXV) ([14]aneN$_4$). Spin-pairing is effected and six-coordinate complexes result when ligands of moderate to strong field strength coordinate in axial positions. High-spin, five-coordinate complexes are obtained from (XXIV) when only ligands of weak field strength (Cl$^-$, Br$^-$, I$^-$) are available for coordination in the axial positions. The difference in stereochemistry is believed to result from the different radii of high-spin and low-spin iron(II). In its low-spin state the ferrous ion is sufficiently small to be accommodated in the in-plane hole of the macrocycle but the somewhat larger high-spin ion is displaced out of the plane and interacts with only one donor species in an axial position. These results have considerable relevance to the function of the naturally occurring iron—porphyrin systems. The conversion of iron(II) from an out-of-plane, high-spin five-coordinate to an in-plane, low-spin six-coordinate species upon oxygenation is typical for the heme proteins myoglobin and hemoglobin and it has been proposed that the structural rearrangements accompanying this change provide the biochemical trigger initiating cooperativity in the protein sub-units with respect to oxygenation [107—109].



(XXIV)



(XXV)

The strong-field bidentate, phenanthroline cannot occupy two axial sites and forces the iron out of the plane in [Fe([14]dieneN$_4$)]$^{2+}$ and the ligand into a folded conformation. The complex [Fe([14]dieneN$_4$)phen][ClO$_4$]$_2$ has a strongly temperature dependent magnetic moment which has been interpreted in terms of a high-spin—low-spin equilibrium [105]. The spin-state of iron(II) in its complexes with the saturated macrocycle (XXV) again depends upon the field strength of the axial ligands, and both low-spin and high-spin species were isolated. With the thiocyanate ion, of intermediate field strength, the complex [Fe([14]ane N$_4$)(NCS)$_2$] was obtained which has a strongly temperature dependent magnetic moment indicative of a transition from the low-spin to the high-spin state at elevated temperatures [106]. Both the low-spin and the high-spin derivatives of (XXV) isolated are six-coordinate. The in-plane hole in this saturated macrocycle is able to accommodate larger metal ions

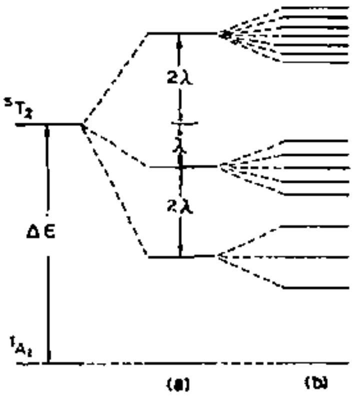


Fig. 5. Effect of (a) spin—orbit coupling and (b) the first order Zeeman effect on the $^5T_2$ and $^1A_1$ terms for iron(II).

than that of (XXIV) thereby allowing high-spin iron to complete its six-coordination.

C. MAGNETIC AND SPECTRAL PROPERTIES

(i) Magnetism

A temperature-induced $^5T_2 \rightleftharpoons {}^1A_1$ transition in a complex should result in a strong temperature dependence of the magnetic moment and a continuous variation from about 5.3 B.M. to approximately 0.6 B.M. might be expected. This has sometimes been observed, but for most of the systems studied variation over the entire range does not occur. In principle, the quantitative description of the temperature dependence of the magnetism would seem to be simple. The $^5T_2$ state, separated from the $^1A_1$ state by an energy difference ΔE, is split by the influence of spin—orbit coupling and the first-order Zeeman effect into three groups of degenerate levels as shown in Fig. 5. Application of the van Vleck equation to a Boltzmann distribution over all sixteen levels leads to the following expression [28,71].

$$\chi_M = \left\{\frac{N\beta^2}{kT}\left[(28x + 9.333)\exp - \left(\frac{\Delta E}{\lambda} - 2\right)x + (22.5x + 4.167)\right.\right.$$
$$\left.\left.\exp - \left(\frac{\Delta E}{\lambda} + 1\right)x + (24.5x - 13.5)\exp - \left(\frac{\Delta E}{\lambda} + 3\right)x\right]\right\}\left\{x\left[1 + 7\right.\right.$$
$$\left.\left.\exp - \left(\frac{\Delta E}{\lambda} - 2\right)x + 5\exp - \left(\frac{\Delta E}{\lambda} + 1\right)x + 3\exp - \left(\frac{\Delta E}{\lambda} + 3\right)x\right]\right\}^{-1}$$

in which $x = \lambda/kT$, λ = spin—orbit coupling constant.

This relatively simple treatment has been singularly unsuccessful in describing spin-transitions in iron(II) and its failure can be ascribed principally to three factors. The first of these is the occurrence of what is virtually a discontinuity in the temperature dependence of the magnetism of systems such as [Fe $phen_2(NCS)_2$], undoubtedly arising from a phase change in the solid. No theoretical model based on a Boltzmann distribution over a number of levels can be expected to be in accord with such behaviour. Secondly, even in systems in which a gradual spin transition occurs the transition is rarely complete and the magnetic moment at low temperatures levels off to values considerably in excess of that expected for low-spin iron(II). A factor further complicating the description of iron(II) crossover phenomena is the apparent temperature dependence of the energy separation between the $^1A_1$ state and the centre of gravity of the $^5T_2$ manifold. The normal, small dependence of the ligand field splitting parameter, Δ, on temperature no doubt contributes to this but of greater significance is the reduction in metal—donor atom distances and concomitant increase in Δ associated with a change from a quintet to a singlet state. Since the excited states will have different but characteristic energy relationships to the ground states, a change in the relative populations of the ground states will be expected to lead to a change in the energy separation between them. A theoretical model which allows for this variation, together with the existence of a fraction of permanently paramagnetic species can reproduce the magnetism of compounds which display a *gradual* spin transition. Harris and Sinn [110] have allowed for a difference in the vibrational partition functions for the two spin states, as was introduced by Ewald et al. [111] in a consideration of the iron(III) dithiocarbamates. It has been pointed out [66] that such a procedure is not very different either conceptually or mathematically to allowing ΔE to vary although this has been challenged by König and Kremer [112]. The assumption of a temperature dependence for ΔE has also been questioned since the expected resulting temperature dependence of ν_{CN} in the infrared spectrum of [Fe $phen_2(NCS)_2$] was not observed [113].

König and Kremer [114] extended the theoretical model to allow for covalency effects and the influence of low-symmetry components in the ligand field. Axial distortion of the octahedron was assumed and an estimate of the axial field splitting of the $^5T_2$ state was obtained directly in some instances from the temperature dependence of the quadrupole splitting in the Mössbauer spectra. Each refinement to the model introduces an additional parameter, and because the treatment is insensitive to fairly wide variations in some of these parameters the quantitative data obtained are of limited value. The failure of any simple model to account adequately for the temperature-dependence of the magnetism of a system which displays a $^5T_2 \rightleftharpoons {}^1A_1$ transition has served to underline the complex nature of crossover phenomena.

(ii) Solid state effects

The crossover situation can presumably exist over a limited range of field strengths only and its manifestation can be expected to be keenly sensitive to

TABLE 5

Influence of crystal polymorph on magnetic properties

Complex	Polymorph	Residual μ (B.M.)	Transition temp. (K)
[Fe $phen_2$ $(NCS)_2$]	I	0.65	174
[Fe $phen_2$ $(NCS)_2$]	II	2.38	174
[Fe $bipy_2$ $(NCS)_2$]	I	0.94	216
[Fe $bipy_2$ $(NCS)_2$]	II	1.39	216
[Fe $bipy_2$ $(NCS)_2$]	III	1.61	210
[Fe $phen_2$ $(NCSe)_2$]	I	0.84	232
[Fe $phen_2$ $(NCSe)_2$]	II	1.65	232

Data taken from Ref. 8.

relatively minor perturbations in the environment about the metal atom. The dependence of the nature of a spin transition on an accompanying phase change has already been noted. There are several other ways in which the course, or indeed the actual occurrence of a spin transition is affected by apparently minor changes in the metal atom environment. Thus in the early examples, [Fe $phen_2(NCS)_2$] and [Fe $bipy_2(NCS)_2$], the magnitude of the residual paramagnetism and the actual transition temperature were found to depend on the particular polymorph being studied (Table 5).

Quite profound effects of the anion associated with a cationic crossover system have been observed. This seems to be a general phenomenon and was initially noted in the salts of [Co $terpy_2]^{2+}$, a d^7 crossover system [80]. The influence of the anion is apparent from the data in Table 6 in which the magnetic properties of various salts of cationic crossover systems are summarised. The effect seems to be arbitrary. In Table 7 are listed the magnetic moments of salts containing three closely related ligands. The particular anion-dependence shown by one complex cation is not necessarily reproduced by a second.

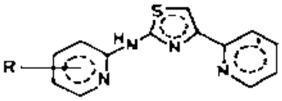
TABLE 6

Influence of the counter anion on the magnetism of cationic iron(II) crossover systems

Complex	μ (B.M.)	Ref.
[Fe pyi_2]Cl_2,$2.5H_2O$	2.82 (293 K); 1.04 (113 K)	71
[Fe pyi_2]SO_4,$2H_2O$	4.08 (293 K); 2.91 (93 K)	71
[Fe $mephen_3$][ClO_4]$_2$	5.39 (294 K); 3.01 (98 K)	62
[Fe $mephen_3$][PF_6]$_2$	5.30 (296 K); 3.91 (92 K)	62
[Fe $paptH_2$][ClO_4]$_2$,H_2O	5.14 (306 K); 4.64 (99 K)	92
[Fe $paptH_2$][NO_3]$_2$,H_2O	3.73 (341 K); 2.19 (287 K)	92
[Fe $paptH_2$]Br_2,$2H_2O$	3.49 (404 K); 1.01 (283 K)	92

TABLE 7

Magnetic moments (B.M.) of salts of $[FeL_2]^{2+}$ L =



Anion	R = H	R = 3-CH_3	R = 4-CH_3
Br^-	2.06 (344 K); 1.01 (283 K)	5.04 (303 K); 3.22 (83 K)	2.13 (343 K); 1.15 (273 K)
NO_3^-	2.44 (301 K); 0.97 (165 K)	5.09 (303 K); 3.63 (83 K)	2.03 (303 K); 0.52 (83 K)
I^-	5.00 (302 K); 4.77 (102 K)	5.10 (303 K); 4.36 (83 K)	1.96 (293 K); 0.90 (83 K)

Data taken from Refs. 92 and 115.

The decisive role the associated anion can play in determining the properties of a cationic crossover system is revealed [102] by the recent structure determination of [Co $terpy_2$]Br_2,$3H_2O$. In this instance it was suggested that either static disorder of one of the anions between different sites or a dynamic, thermally stimulated interchange of the anion between two closely adjacent lattice sites of comparable energy contributes significantly to the manifestation of the spin transition.

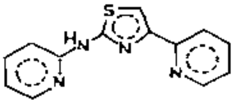
The role of lattice forces is shown by the properties of the solvates of [Fe $papt_2$] (Table 8) which differ significantly from those of the unsolvated material. Similarly, while [Fe $dimephen_2(NCS)_2$] and its α-picoline solvate display an abrupt transition, the pyridine solvate remains high-spin [35] over the range 293—80.5 K. Variation in the extent of hydration has also been found to affect the properties of crossover systems [71,92].

The change in magnetism sometimes noted on dissolution of a complex is a reflection of the relaxation of the constraints which may be imposed by the crystal lattice. Jesson et al. [104] observed a favouring of the low-spin state in solid iron(II) poly(pyrazolyl)borate complexes and rationalised this in terms of an additional component to the crystal field due to packing in the lattice. But the contribution of the lattice can act in reverse. Thus for bis(2-(1,10-phenanthrolin-2-yl)thiazolidine iron(II) fluoroborate moments of 4.7 and 2.9 B.M. at 290 K were observed for the solid and a solution in nitromethane, respectively [95].

Residual paramagnetism, due to a fraction of molecules permanently in the

TABLE 8

Magnetic moments (B.M.) of [Fe(L — H$)_2$] and its solvates L =



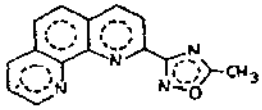
Complex	T = 297 K	T = 94 K
[Fe(L — H$)_2$]	4.96	1.55
[Fe(L — H$)_2$]C_6H_6	4.92	4.29
[Fe(L — H$)_2$]$\frac{4}{3}CHCl_3$	5.02	4.58

Data taken from Ref. 93.

TABLE 9

Time dependence of the magnetism of $[FeL_2][BF_4]_2$

L =



Time (weeks)	10^6 χ'_M (c.g.s.)		μ (B.M.)	
	303 K	83 K	303 K	83 K
0	11600	19700	5.34	3.63
1	11200	17900	5.23	3.46
3	11400	15900	5.28	3.26
8	11200	13700	5.23	3.03
17	11300	12700	5.17	2.91
50	10800	5000	5.13	1.89

high-spin state, is generally associated with a ${}^5T_2 \rightleftharpoons {}^1A_1$ transition in iron(II) and is a lattice effect. This has been shown conclusively for the complex [Fe $papt_2$] and its chloroform solvate. In the unsolvated complex approximately 17% of the complex remains high-spin even at 4.2 K, whereas for the chloroform solvate the residual paramagnetism is much higher and approximately 52% of the molecules do not undergo the spin change [116]. Mössbauer effect studies of vitreous solutions of the complex show, however, that in solution the transition proceeds to completion [117]. The retention of a fraction of molecules in the ${}^5T_2$ state in solid samples is presumably necessary to maintain lattice stability. A given lattice may be expected to have only limited tolerance for the changes in intramolecular dimensions which accompany the spin-state change.

A different, though related, manifestation of the influence of lattice forces on the course of a spin transition has been noted for bis(3-(1,10-phenanthrolin-2-yl)-5-methyl-1,2,4-oxadiazole)iron(II) fluoroborate, containing the tridentate (XX) [97]. This complex undergoes a thermally induced spin transition which is incomplete in the sense that there is a significant residual paramagnetism. The unique feature of this system, however, is the time-dependence of the magnitude of the contribution of "permanently" high-spin material to the magnetism (Table 9). As the sample ages the conversion to the ${}^1A_1$ state proceeds to a greater extent. The origins of this time-dependence are not clear but it is suggested that it is associated with some slow, apparently minor modification of the crystal lattice which allows an increased concentration of the low-spin species at low temperatures. Time-dependence of the magnetism has also been noted in the crossover systems [Fe $pyim_2$] $[ClO_4]_2$ (ref. 74), [Fe $paptH_2$]$(NO_3)_2$ (ref. 92) and [Fe $phen_2(NCS)_2$] (ref. 29), although in these instances it does not relate to the residual paramagnetism. Such lattice effects as these are unpredictable and introduce what would seem to be an unsurmountable barrier to the derivation of a precise and generally applicable theoretical description of the crossover phenomenon in solids.

(iii) Mössbauer spectral data

Although magnetic data provide a convenient means for detecting a spin transition, the information obtained merely represents an average of the magnetism for all the states involved. Ideally, the identification of a spin transition requires the concurrent observation of properties characteristic of the high-spin and low-spin states separately. The Mössbauer effect is ideal in this respect since it allows a ready distinction between the low- and high-spin forms of iron(II). Characteristically the spectra of S=0 Fe(II) ions show an isomer shift, δ_{IS}, in the range 0.0—+0.4 mm s^{-1} (with respect to natural iron) and a quadrupole splitting, ΔE_Q, which is strongly dependent on the metal ion environment but for complexes of imine-type ligands is generally in the range 0.0—1.0 mm s^{-1}. For S=2 Fe(II) ions δ_{IS} is about 1.3 mm s^{-1} and ΔE_Q is in the range 2.5—3.5 mm s^{-1}. The observation of separate Mössbauer spectra for the two spin states involved in a transition requires a relaxation time for the spin transition greater than the precession time of the ^{57}Fe nucleus ($<10^{-7}$ s). Rate constants for the conversions represented by $^5T_2 \rightleftharpoons {}^1A_1$ have been estimated as about 10^7 s^{-1} by Beattie et al. [118] for the transition occurring in the tris(polypyrazolyl)borate iron(II) complex *in solution*. Because of the structural changes concomitant with the change in spin-state and of the obvious influence of lattice effects on the course of a spin transition, a fast dynamic conversion as observed in solution seems unlikely for solid systems and the observance of Mössbauer spectral features characteristic for both $^5T_2$ and $^1A_1$ states of iron(II) is to be expected. In the extensively studied tris(N,N-dialkyldithiocarbamato)iron(III) chelates, d^5 crossover systems, only *average* spectra were observed [119] and this was attributed to very rapid interconversion of the spin isomers. However, this interpretation has recently been challenged by Merrithew and Rasmussen [4] who consider that the nature of the temperature dependence of the Mössbauer quadrupole splittings is not in accord with a "spin equilibrium". These systems have been brought further into question by recent structural studies [5] on tris(N,N-diethyldithiocarbamato)iron(III). Mössbauer effect measurements have positively established the co-existence of high- and low-spin iron(III) in other systems [120].

Mössbauer spectral data have been obtained for a large number of iron(II) crossover systems and in all instances provide clear evidence for a spin-transition. In general the spectra have been recorded at two temperatures, the higher corresponding usually to almost complete occupancy of the $^5T_2$ state and the lower to the $^1A_1$ state. The data are collected in Table 10. Inspection of these data reveals a generally large quadrupole splitting in the $^5T_2$ state spectra and, particularly for the complexes derived from certain of the tridentate chelating agents, unusually large quadrupole splitting in the $^1A_1$ state spectra. In almost all these complexes distortions from regular octahedral symmetry must be considerable, and the deviation can be expected to be greatest in the conjugated tridentate chelating agents because of their more rigid stereochemical demands.

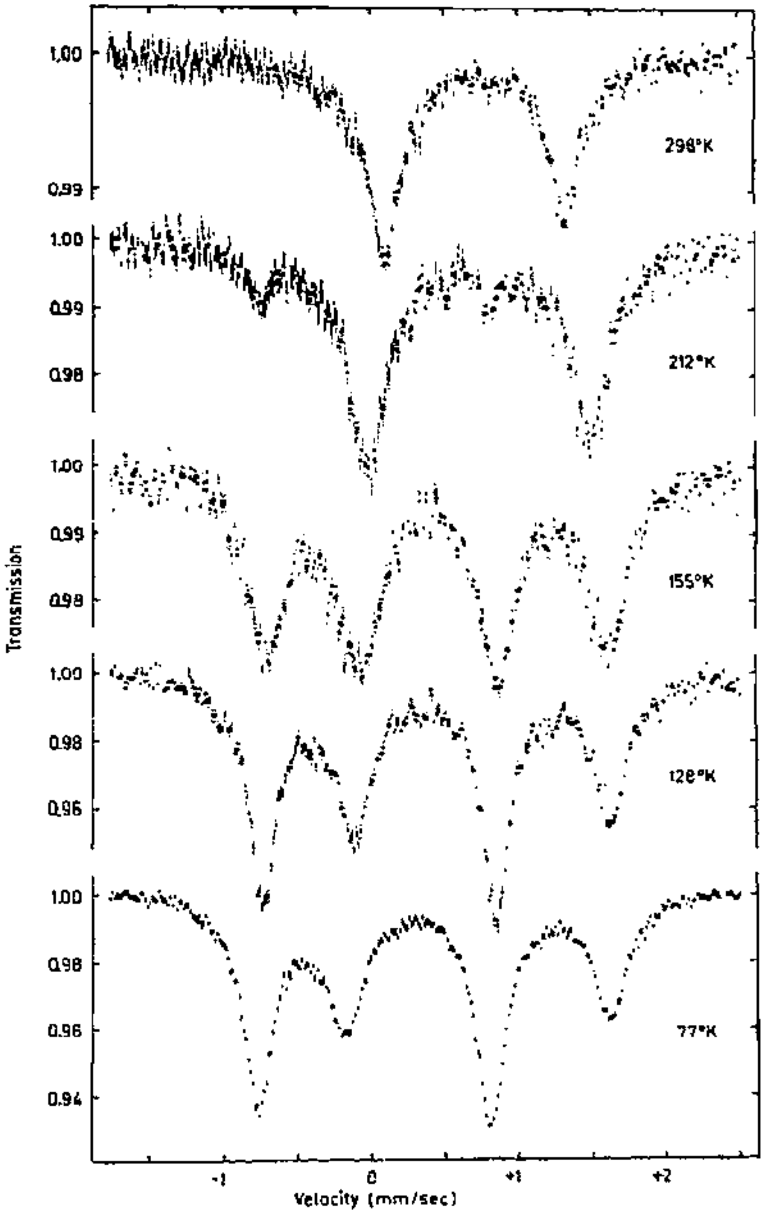


Fig. 6. Temperature dependence of the Mössbauer spectrum of [Fe pythiaz$_2$][BF$_4$]$_2$ (reproduced from ref. 122 by permission of North-Holland Publishing Company, Amsterdam).

Several systems have been studied in detail at a number of temperatures which include the range within which the spin transition occurs [36,63,64, 104,116,121,122]. The diagnostic value of the Mössbauer effect is well revealed by the data obtained for the compound [Fe pythiaz$_2$][BF$_4$]$_2$. The magnetic

TABLE 10

Mössbauer spectral data for iron(II) crossover systems

Complex	T (K)	State	ΔE_Q	$\delta_{\mathrm{i.s.}}^{a}$	Ref.
[Fe phen$_2$(NCS)$_2$]	293	$^5T_2$	2.67	0.98	28
	77	$^1A_1$	0.34	0.37	28
[Fe phen$_2$(NCSe)$_2$]	293	$^5T_2$	2.52	1.03	28
	77	$^1A_1$	0.18	0.35	28
[Fe phen py$_2$(NCS)$_2$]	298	$^5T_2$	2.46	0.91	49
	77	$^1A_1$	0.28	0.38	49
[Fe bipy$_2$(NCS)$_2$]	293	$^5T_2$	2.18	1.06	27
	77	$^1A_1$	0.50	0.36	27
[Fe 5-Clphen$_2$(NCS)$_2$]	300	$^5T_2$	2.73		37
	77	$^1A_1$	0.295		37
[Fe 5-mephen$_2$(NCS)$_2$]	300	$^5T_2$	2.55		37
	77	$^1A_1$	0.41		37
[Fe 5-phphen$_2$(NCS)$_2$]	77	$^1A_1$	0.36		37
[Fe 5-NO$_2$phen$_2$(NCS)$_2$]	300	$^5T_2$	2.67		37
	77	$^1A_1$	0.34		37
[Fe dimephen$_2$(NCS)$_2$]	298	$^5T_2$	2.59	0.97	36
	88	$^1A_1$	0.46	0.34	36
[Fe dimebipy$_2$(NCS)$_2$]	300	$^5T_2$	2.68		37
	77	$^1A_1$	0.37		37
[Fe ppi$_2$(NCS)$_2$]	298	$^5T_2$	2.48	0.93	52
	298	$^1A_1$	0.39	0.25	52
	4.2	$^5T_2$	3.08	0.96	52
	4.2	$^1A_1$	0.40	0.29	52
[Fe pyim$_3$][ClO$_4$]$_2$	294	$^5T_2$	2.29	1.02	74
	80	$^5T_2$	2.69	1.10	74
	80	$^1A_1$	0.75	0.45	74
[Fe pyi$_3$]Cl$_2$	295	$^5T_2$	2.30	0.90	71
	295	$^1A_1$	0.44	0.35	71
	77	$^1A_1$	0.48	0.44	71
[Fe pbi$_3$][ClO$_4$]$_2$	293	$^5T_2$	2.21	0.99	75
	293	$^1A_1$	0.42	0.49	75
	80	$^5T_2$	2.60	1.13	75
	80	$^1A_1$	0.49	0.50	75
[Fe mephen$_3$][ClO$_4$]$_2$	295	$^5T_2$	1.03	0.95	63
	77	$^5T_2$	1.96	1.01	63
	77	$^1A_1$	0.56	0.39	63
[Fe picam$_3$]Cl$_2$	298	$^5T_2$	2.04	0.98	84
	77	$^1A_1$	0.55	0.52	84
[Fe(HB(dimepz)$_3$)$_2$]	298	$^5T_2$	3.74	1.04	104
	77	$^1A_1$		0.48	104
[Fe ppa$_2$]I$_2$	300	$^1A_1$	1.24	0.27	86
[Fe pythiaz$_2$][BF$_4$]$_2$	298	$^5T_2$	1.29	0.93	122
	86	$^5T_2$	1.84	0.96	122
	86	$^1A_1$	1.60	0.26	122

TABLE 10 (continued)

Complex	T(K)	State	ΔE_Q	$\delta^a_{I.S.}$	Ref.
[Fe papt$_2$]	305	$^5T_2$	2.10	0.89	116
	90	$^5T_2$	2.20	0.91	116
	90	$^1A_1$	1.57	0.33	116
[Fe pbbt$_2$][ClO$_4$]$_2$	300	$^5T_2$	2.16	0.88	123
	90	$^1A_1$	1.19	0.39	123
[Fe pphy$_2$][BF$_4$]$_2$	306	$^5T_2$	0.7	0.91	124
	250	$^1A_1$	1.64	0.24	124
[Fe pbuti$_2$][BF$_4$]$_2$	306	$^5T_2$	1.2	0.90	124
	98	$^1A_1$	1.41	0.26	124
[Fe isoxazole$_6$][ClO$_4$]$_2$	215	$^5T_2$	1.62	1.35 [b]	125
	180	$^1A_1$		0.72	125

[a] Relative to natural iron.
[b] Reference material for $\delta_{I.S.}$ not quoted.

moment of this compound decreases gradually from 5.53 B.M. at 298 K to 3.21 B.M. at 80 K and is clearly levelling out to a value of about 3 B.M. at low temperatures. Because of this high residual paramagnetism, the magnetic data in this instance do not alone allow a distinction between an incomplete quintet—singlet transition and a virtually complete quintet—triplet transition [94]. The spectra shown in Fig. 6 illustrate, however, how clearly the Mössbauer effect resolves the nature of the transition. At 298 K the spectrum of [Fe pythiaz$_2$][BF$_4$]$_2$ consists of a single doublet, characterised by ΔE_Q = 1.29 mm s^{-1} and assigned to the quintet state [122]. At 212 K a second doublet is clearly visible and this is assigned to the singlet state. Interestingly, both doublets fortuitously show the same quadrupole splitting, the high value for the singlet state being indicative of gross distortion from O_h symmetry. As the temperature is lowered further the intensity of the quintet contribution decreases while that of the singlet increases. Below about 112 K the ratio of the intensities remains almost constant, indicating the persistence of a mixture of the two spin states and consistent with the value for the residual paramagnetism. Even at 4.2 K the ratio is little changed. Thus the residual paramagnetism clearly arises from an incomplete quintet—singlet transition. In other instances too the Mössbauer effect has clearly differentiated possible quintet—triplet and quintet—singlet transitions [51,52]. Taken in conjunction with magnetic data, the temperature-dependence of the Mössbauer spectra may be used to evaluate the Debye—Waller factors for the solids in either the $^5T_2$ or $^1A_1$ state. In fact different values for the two spin isomers have been found, [36,116,122,126] underlining the interdependence of lattice forces and the occurrence of a spin transition

(iv) Infrared spectral data

The observation of features characteristic of the separate quintet and singlet states in Mössbauer spectra of crossover systems indicates that infrared spectra

TABLE 11

Infrared data for $[FeL_2(NCS)_2]$

Complex	ν (cm^{-1}) ($^5T_2$; 298 K)	ν (cm^{-1}) ($^1A_1$; 100 K)	Assignment
$[Fe\ bipy_2(NCS)_2]$	235	393.0; 374.7	Fe—N (bipy)
$[Fe\ bipy_2(NCS)_2]$	253	498.3; 492.0	Fe—N (NCS)
$[Fe\ phen_2(NCS)_2]$	220	379.0; 371.0	Fe—N (phen)
$[Fe\ phen_2(NCS)_2]$	252	532.6; 528.5	Fe—N (NCS)

Data taken from Refs. 127 and 128.

should also reveal the separate existence of the two spin states since the periods of nuclear oscillations are of the order of 10^{-13} s. The contraction in the metal—donor atom distances accompanying a change in ground-state from $^5T_2$ to $^1A_1$ would be expected to lead to a shift to higher energies of the metal—donor atom stretching modes and displacements of the frequencies associated with modes involving only the ligand atoms.

Detailed infrared spectral studies of iron(II) crossover systems have been confined almost entirely to the $[Fe\ phen_2X_2]$ or $[Fe\ bipy_2X_2]$ complexes. König [8] has considered much of the infrared data for these systems and since the appearance of his review some significant results using isotopically enriched ^{57}Fe and ^{54}Fe samples have been obtained [127—129]. The use of the metal isotope technique [130] has enabled the positive identification of the metal—nitrogen stretching vibrations involving both the heterocyclic and thiocyanate nitrogen atoms. The results, summarised in Table 11, show a marked shift to higher frequencies for the metal—donor atom vibrations with the change from the quintet to the singlet ground state. Contrary to the previous conclusions of König and Madeja [131], this change implies a strengthening of both the Fe—N (amine) and Fe—N (NCS) bonds, consistent with the bond shortening revealed by the structure determinations [30].

The data in Table 11 were obtained from measurements at about 298 K and 105 K, at which temperatures the complexes are almost entirely in the quintet or singlet ground state, respectively. Data have also been obtained over a range of temperatures, including the transition region, and these clearly show the separate existence of molecules in the two ground states [26,113].

D. THERMODYNAMIC ASPECTS

In the early reports of a spin transition the change in spin state was discussed in terms of a "spin equilibrium" involving the nearly equi-energetic $^5T_2$ and $^1A_1$ states. That such transitions do not involve a simple equilibrium was soon established by the failure of attempts to describe the phenomena quantitatively. In particular, non-linear plots of ln K vs $1/T$ were obtained where K

is the equilibrium constant for the processes [70,92,105,106]

low-spin ⇌ high-spin

Relative concentrations of the low-spin and high-spin species could be extracted from the magnetic data at various temperatures. This empirical treatment of a "spin equilibrium" is, as Machado [11] has pointed out, equivalent to the description in terms of the van Vleck equation. The failure of both approaches seems to lie in the intramolecular and macroscopic structural changes accompanying the spin transition.

A true equilibrium seems to be involved in the spin transition exhibited by $Fe[HB(pz)_3]_2$ *in solution* [103]. The molar free-energy change for the process, ΔG, was obtained from the magnetic data according to the expression

$$\Delta G = RT \ln\left[\frac{\mu^2_{\mathrm{H.S.}}}{\mu^2} - 1\right]$$

where $\mu_{\mathrm{H.S.}}$ was taken as 5.22 B.M., the value found for a similar, completely high-spin complex, and μ was the observed moment of the equilibrium mixture at temperature T. A plot of ΔG vs T was found to be essentially linear over the experimental temperature range and values of $\Delta H = 16.11$ kJ mol^{-1} and $\Delta S = 47.7$ JK^{-1} mol^{-1} were obtained. The apparent success of a simple analysis in this instance can be ascribed to the absence of the lattice effects which influence markedly the behaviour of solids.

Sorai and Seki [113] have observed a jump in the heat capacity of [Fe $phen_2(NCS)_2$] and [Fe $phen_2(NCSe)_2$] at their magnetic transition temperatures and from the temperature dependence of the heat capacities determined the enthalpy and entropy of transition (Table 12). It is noteworthy that the transition entropies are almost the same for each compound and moreover are very close to the value found for the polypyrazolyl borate system in solution. The entropy term includes a contribution of $R \ln 5 = 13.38$ JK^{-1} mol^{-1} due to the spin degeneracy of the quintet state. The excess entropy was accounted for in terms of enhanced phonon excitation in the quintet state [113]. König and Ritter [132] suggested, however, that the vibrational contribution to the entropy will not be large and the configurational entropy, associated with the geometrical changes in the Fe—N_6 core occurring with the transition, will

TABLE 12

Thermodynamic data for the magnetic phase transition in [Fe $phen_2$ X_2]

Complex	T_c (K)	ΔH (kJ mol^{-1})	ΔS (JK^{-1} mol^{-1})
[Fe $phen_2(NCS)_2$]	176.29	8.60	48.78
[Fe $phen_2(NCSe)_2$]	231.26	11.60	51.22

Data taken from Ref. 113.

make the major contribution. This is supported by the near-equality of the entropy terms found for the transitions in solid [Fe phen$_2$(NCS)$_2$] and in [Fe(HB(pz)$_3$)$_2$] in solution, and by a detailed study of the Debye—Waller factors for [Fe dimephen$_2$(NCS)$_2$] in the transition region [36].

The results of Sorai and Seki clearly demonstrate the cooperative nature of spin transition in the solid state. It would seem that it is a treatment of the transition in terms of cooperative phenomena which holds the greatest promise for a meaningful theoretical understanding of the crossover behaviour in solids. Bari and Sivardière [133] showed that a modified molecular-field model, as developed by Chesnut [134] to account for the singlet—triplet transition in certain ion-radical salts of tetracyanoquinomethane, when applied to d^6 crossover systems can describe the gross features of $^5T_2 \rightleftharpoons {}^1A_1$ transitions. Either a gradual or abrupt (first order phase change) transition can be reproduced by this model, depending on the values of the parameters chosen. Chesnut has further shown that relatively minor changes in a system which shows no phase change may result in the appearance of such a change.

E. CONDITIONS FOR A $^5T_2 \rightleftharpoons {}^1A_1$ TRANSITION

The condition that the mean pairing energy for the metal ion d electrons (π) and the ligand field splitting energy (Δ) must be nearly equal in order for a spin crossover to occur hardly seems compatible with the considerable number of instances of spin transitions now known. Griffith [135] in 1956, commented that, because of spin—orbit coupling and small departures from cubic symmetry, the criterion $\Delta > \pi$ leads to a low-spin state is valid only if $|\Delta - \pi|$ is sufficiently large — perhaps greater than 2000 cm^{-1} for the first transition series ions. If $|\Delta - \pi| < 2000$ cm^{-1} an appreciable concentration of both spin forms at room temperature is to be expected. The spin-pairing energy for Fe(II) in an octahedral environment has been calculated [136] but, because of the different radii for the metal in the high-spin and low-spin states, the field strength near the crossover depends on the spin state. It has been pointed out [111] that a necessary and general condition for the existence of equienergetic ground states is:

$$\Delta_{\mathrm{H.S.}} < \pi < \Delta_{\mathrm{L.S.}}$$

Direct evaluation of either $\Delta_{\mathrm{H.S.}}$ or $\Delta_{\mathrm{L.S.}}$ from the electronic spectra of Fe(II) crossover systems is, in general, not feasible, since the d—d transitions tend to be obscured by charge-transfer absorption, particularly in systems containing highly conjugated ligands. Nevertheless, a reasonable estimate of Δ may be obtained from the spectra of the corresponding Ni(II) complexes since for these the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition is generally well resolved. Robinson et al. [137], who first drew attention to the relationship between Δ(Ni(II)) and the spin-state of the related Fe(II) complex, established a range of Δ of 11600—13400 cm^{-1} within which the critical value at the crossover should lie (this would correspond to the approach of the crossover from the weak field side). This range was later narrowed by Nelson and Rodgers [83]. Although inconsistencies have been observed [95] and caution must be exercised in applying this relationship between Δ(Ni(II)) and the spin-state of Fe(II), it does provide a very useful indication of the likely behaviour of the Fe(II) complex. In at least one instance [86] it has led directly to the recognition of crossover behaviour in an apparently low-spin complex.

F. CONCLUDING REMARKS

In almost all instances, quintet—singlet transitions in compounds of iron(II) have been detected by the observation of anomalous magnetism. Two apparently distinct kinds of transition are revealed by the magnetic properties of iron(II) "crossover" systems:

(a) those in which the change in ground state is abrupt, occurring within a very narrow temperature range, and

(b) those in which the proportion of molecules in the two ground states varies gradually over an extended range of temperature.

The course of a spin transition is determined by whether or not it accompanies (or in fact instigates) a first-order phase transition which leads to behaviour of the first kind. In either instance the transition $^5T_2$—$^1A_1$ may or may not be complete at low temperatures. In the latter case a proportion of molecules remains in the high-spin state and contributes to a residual paramagnetism, the magnitude of which is closely dependent on the physical state of the "crossover" species. For one system it has been shown from Mössbauer effect studies that the residual high-spin fraction disappears altogether in solution [117].

Magnetic data alone do not characterise a spin transition and this is particularly so for those systems which display a large residual paramagnetism. For these the involvement of a triplet-state species cannot a priori be excluded. However, the Mössbauer effect has been able to resolve this difficulty in the systems so far studied since it has revealed the retention of a constant fraction of quintet-state species.

Despite the number of crossover Fe(II) systems known, none of these contains the metal in a regular octahedral environment, and in fact in some of them the actual symmetry is probably quite low (the usual procedure of adopting the nomenclature of O_h symmetry has, nevertheless, been followed in this review). Machado [12] has drawn attention to the importance of the ligand structure in influencing the symmetry of the metal ion environment and, thereby, the occurrence of a spin transition. The degeneracy of the $^5T_2$ state is lifted by the introduction of low-symmetry components into the ligand field [114,138,139] and this will contribute to a breakdown of the energy barrier separating the two spin states [114,126]. A spin transition has recently been reported [125] in hexakis(isoxazole)iron(II) perchlorate and this system may be one in which distortion from O_h symmetry is minimal. Structural data for this complex would be of considerable significance. Obviously the further understanding of the crossover phenomenon and of the influence of lattice forces and distortion effects on its manifestation will require much more detailed structural information than is presently available, particularly at temperatures both above and below the transition region. In addition, detailed studies for systems in solution are necessary to allow a more reasonable assessment of the importance of lattice effects and of the energetics of the spin transition.

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