Coordination Chemistry Reviews
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

SOME ASPECTS OF THE CHEMISTRY OF BIS(2,2′-DIPYRIDYL) AND BIS(1,10-PHENANTHROLINE) COMPLEXES OF IRON(II)

EDGAR KÖNIG

Institut für Physikalische Chemie II, Universität Erlangen-Nürnberg, Erlangen (Germany)

(Received June 4th, 1968)

CONTENTS

A. INTRODUCTION

The bidentate heterocyclic diamines 2,2′-dipyridyl (dip) and 1,10-phenanthroline (phen) among the best coordinating agents known, were introduced by Blau[1,2] in 1888. A review covering the more classic work on the metal complexes of these and of related ligands was published by Brandt, Dwyer, and Gyarfas[3] in 1954. The numerous diimine compounds of iron(II), cobalt(II), and nickel(II) prepared since then were reviewed recently in this journal[4] and some additional information, with particular emphasis on electronic spectral properties, may be found in a book by Jørgensen[5].

Within the first transition metal series, the tris(2,2′-dipyridyl) complexes of chromium (II) and iron(II) assume low-spin ground states, whereas the complexes of the remaining bivalent metals (*viz.* Mn^{II}, Co^{II} and, of course, V^{II}, Ni^{II} and Cu^{II}) are of the high-spin type[6,7]. The corresponding phenanthroline compounds have similar properties to their 2,2′-dipyridyl analogs. Both high-spin ($^5T_2$) and low-spin

($^1A_1$) ground states may be observed with one particular transition metal ion if mixed complexes are considered. The ability to form high-spin and low-spin complexes with different metal ions seems to be a consequence of the position of the dip and phen ligands in the spectrochemical series, giving rise to a field strength slightly higher than that of ethylenediamine (en).

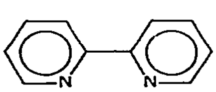
The consecutive formation constants of complex ions usually decrease in magnitude according to $K_1 > K_2 > \ldots > K_n$. However, in the iron(II) dipyridyl and phenanthroline systems in aqueous solution, Irving and Mellor[8] determined the formation constants

$$\begin{array}{llll} \text{Fe}^{\text{II}}\text{-dip:} & K_1 = 16000, & K_2 = 5000, & K_3 = 8\times 10^7 \\ \text{Fe}^{\text{II}}\text{-phen:} & K_1 = 7\times 10^5, & K_2 = 2\times 10^5, & K_3 = 10^{10}. \end{array}$$

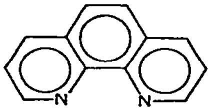
It has been concluded that the much larger K_3 is caused by the increase in stability upon spin-pairing and that $[\text{Fe dip}_2(\text{H}_2\text{O})_2]^{2+}$ and $[\text{Fe phen}_2(\text{H}_2\text{O})_2]^{2+}$ should be high-spin ions. The change from a d^6 high-spin (quintet) to a d^6 low-spin (singlet) ground state thus takes place within the series of $[\text{Fe dip}_2\text{X}_2]$ and $[\text{Fe phen}_2\text{X}_2]$ complexes[9]. Considerable effort has centered around the synthesis and study of compounds with ligands X covering a wide range of ligand field strengths. Since only two ligand positions are varied through the spectrochemical series, the average ligand field changes in rather small steps. It may be expected that, somewhere between the high-spin compounds at the low-field limit and the low-spin compounds at the high-field limit, the two ground states of different multiplicity become almost equi-energetic. The series of complexes reviewed here is thus particularly useful in a study of the properties which arise in the neighborhood of the cross-over point.

B. PREPARATIVE METHODS AND CHEMICAL PROPERTIES

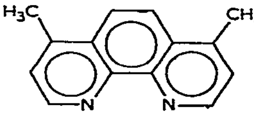
The mixed ligand complexes of iron(II) considered below are essentially of two types: $[\text{Fe(NN)}_2\text{X}_2]$, where X is an unidentate anionic ligand, and $[\text{Fe(NN)}_2\text{(AA)}]$, where AA is a bidentate dianionic ligand. The bidentate heterocyclic ligands NN employed include 2,2′-dipyridyl (dip; I), 1,10-phenanthroline (phen; II), and 4,7-dimethyl-1,10-phenanthroline (4,7-dmph; III)



(I)



(II)



(III)

The most complete series at the time of writing is the series of *bis* (1,10-phenanthroline) complexes. Thus $[\text{Fe phen}_2\text{X}_2]$ complexes (in case of bidentate ligands AA we take $X = \frac{1}{2}(AA)$) have been prepared with all those ligands X in the spectrochemical series which are italicied below (where more than one ligating atom exists, the atom directly coordinated to the central ion has been underlined)

$$\begin{aligned}
&I^- < Br^- < Cl^- \sim \mathrm{\underline{S}CN^-} \sim N_3{}^- < F^- < \mathrm{\underline{O}C(NH_2)_2} < \mathrm{OH^-} \sim \\
&HCO\underline{O}^- \sim CH_3CO\underline{O}^- < (CO\underline{O})_2{}^{--} \sim \mathrm{H_2O} \sim \underline{O}OCCH_2CO\underline{O}^{--} < \\
&\underline{N}CO^- < \underline{N}CS^- \sim \underline{N}CSe^- < \mathrm{NH_3} \sim \mathrm{C_5H_5N} < \\
&\mathrm{\underline{N}H_2CH_2CH_2\underline{N}H_2} < \mathrm{dip} \sim phen < \underline{N}O_2{}^- < \underline{C}NO^- < CN^- .
\end{aligned} \tag{1}$$

As far as is known, most of the properties of compounds within the series [Fe $\mathrm{dip_2X_2}$] and [Fe $\mathrm{(4,7\text{-}dmph)_2X_2}$] resemble the properties of the corresponding [Fe $\mathrm{phen_2X_2}$] compounds. Therefore, in general, reference will only be made to the latter. Exceptions occur where additional information results by considering compounds within the other two series.

Owing to the preferred formation of the low-spin *tris* complex it is expected that, in aqueous solution, those complexes [Fe $\mathrm{phen_2X_2}$] should be stable where the ligand field strength of X is sufficiently high to effect the pairing of spins. In fact, only the diamagnetic compounds [Fe $\mathrm{phen_2(CN)_2}$] and [Fe $\mathrm{phen_2(CNO)_2}$] as well as the border-line complex [Fe $\mathrm{phen_2(NCS)_2}$] have been isolated from aqueous media[10–12].

Attempts by Hieber[13] and by Basolo and Dwyer[14] to prepare high-spin [Fe $\mathrm{phen_2X_2}$] complexes employed the thermal cleavage of the corresponding [Fe $\mathrm{phen_3}$]$\mathrm{X_2}$ compounds. However, it has been realized only recently[15–17] that in most cases completely pure products cannot be obtained by this procedure. Two improved methods are currently in use for the effective preparation of the various bis(diamine) complexes:

(i) Cleavage of the corresponding tris(diamine) complexes which may be achieved by several procedures:

(a) Pyrolysis is the only method available for the preparation[17] of [Fe $\mathrm{phen_2I_2}$], all other procedures having proved unsuccessful[15,16]. [Fe $\mathrm{phen_3}$]$\mathrm{I_2}$ requires heating *in vacuo* at 186° for 7 days.

(b) Thermal decomposition under moderate conditions takes place if the *tris* complex is suspended in an inert solvent under reflux conditions. The compounds [Fe $\mathrm{phen_2X_2}$] with X = Cl, Br, $\mathrm{N_3}$, NCO, NCS, NCSe, and HCOO have been prepared by this method[15,16]. Acetone, chloroform, tetrahydrofuran, dioxane, benzene and xylene were used as solvents by one group of workers[15,16], carbon tetrachloride and methylcyclohexane by another group[17].

(c) The extraction method removes the diamine resulting from the dissociative equilibrium of the tris(diamine) complex. In this way [Fe $\mathrm{phen_2X_2}$] compounds with X = Cl, Br, $\mathrm{N_3}$, NCO, NCS, NCSe, and HCOO have been obtained[15,16]. If certain solvents (*e.g.* pyridine, to a lesser extent picoline, dimethylformamide, and acetonitrile) are employed, this procedure yields the compounds in a crystalline form.

(ii) Reaction of anhydrous iron(II) salts with the diamine in suitable solvents. This reaction takes place in solvents which show a low solvating ability towards the anion and small values of the dielectric constant. The exchange of pyridine in [Fe py_4X_2] compounds for bidentate diamines like 1,10-phenanthroline is favoured by a large entropy effect. In this way the complexes [Fe $phen_2X_2$], where X = Cl, Br, N_3, NCO, NCS, NCSe, HCOO, and CH_3COO have been prepared[15,16].

Finally, complexes having the intermediate $^3T_1$ (S = 1) ground electronic state are obtained by reacting iron(II) fluoride, FeF_2, iron(II) oxalate, Fe(ox), and the pyridine adduct of iron(II) malonate, Fe(mal) · py · H_2O, with the diamine. Employing, *e.g.*, 1,10-phenanthroline, the *tris* complexes [Fe $phen_3]X_2$, where X = F, ½(ox), and ½(mal), are formed in a first step. On precipitation with acetone, the corresponding *bis* complexes, [Fe $phen_2X_2$] are obtained[15,18].

In water and methanol, most high-spin *bis* complexes dissociate almost immediately and thus the equilibrium

$$3[\text{Fe phen}_2\text{X}_2] + n\text{solvent} \rightleftharpoons 2[\text{Fe phen}_3]\text{X}_2 + \text{FeX}_2 \cdot n(\text{solvent}) \qquad (2)$$

is shifted far to the right. Exceptions occur for the compounds prepared according to the last method, since complexes with intermediate spin decompose only slowly in these solvents. On the other hand, it has been shown[16] by application of Job's method[19] to the particular case of [Fe $phen_2Cl_2$] that, in pyridine, the formation of the *bis* complex is favoured and thus eq. (2) is shifted to the left, *cf.* preparation (i, c) listed above.

The compound [Fe $phen_2(CN)_2$] (and, likewise, the compound [Fe $dip_2(CN)_2$]) shows appreciable dibasic character and reacts reversibly with acids to yield stable protonated derivatives[10,20]. Hamer and Orgel[21] have demonstrated that it is the coordinated cyano groups that are protonated thus forming the [Fe $phen_2(C{\equiv}NH)_2]^{2+}$ ion. Similar behaviour has been observed[11] with [Fe $phen_2(CNO)_2$]. Quite generally, Lewis acids react with [Fe $phen_2(CN)_2$] to form simple addition compounds[22,22a,22b]. The subject has been reviewed recently by Shriver[22c]. The thiocyanato complex [Fe $phen_2(NCS)_2$] reacts with dry hydrogen chloride forming adducts which contain about four molar equivalents of hydrogen chloride[12]. However, no evidence has been found that protonation of the coordinated thiocyanato groups has occurred.

Several [Fe $phen_2X_2$] compounds may be oxidized readily to yield the corresponding complexes of iron(III). Thus if concentrated nitric acid is added to [Fe $phen_2(CN)_2$], the complex [Fe $phen_2(CN)_2]NO_3 \cdot 4H_2O$ may be crystallized from the resulting solution[10]. Likewise, the compounds where X = Cl and X = Br may be oxidized with chlorine and bromine respectively[23] to form the complexes [Fe $phen_2Cl_2$]Cl and [Fe $phen_2Br_2$]Br.

Attempts to determine molecular weights and dipole moments of the high-spin *bis* complexes have been unsuccessful since no solvents other than those which cause decomposition have been found. However, the slow dissociation of the low-spin compounds as well as of the compounds with the $^3T_1$ ground states may be used to obtain at least some approximate data on solutions of these complexes. Thus the molecular weight of [Fe $phen_2F_2$] has been measured[15] in aqueous solution (found: 377, calcd: 454.3). The molar conductivities Λ of several complexes have been studied[11,15] and the results are listed in Table 1. The values of Λ are basically in agreement with the non-electrolyte character of the compounds, although appreciable dissociation is suggested.

TABLE 1

MOLAR CONDUCTIVITIES OF [Fe $phen_2X_2$] COMPOUNDS

Compound	*Solvent*	Λ, *mho cm*^{2} *mole*$^{-1}$
[Fe $phen_2(CNO)_2$] · H_2O	$(CH_3)_2SO$	2.5
[Fe $phen_2$ox] · $5H_2O$	CH_3OH	15.2
[Fe $phen_2$mal] · $7H_2O$	CH_3OH	21.6
[Fe $phen_2F_2$] · $4H_2O$	CH_3OH	43.1

C. RESULTS OF INVESTIGATIONS BY PHYSICAL METHODS

The configuration $[Ar](3d)^6$ of iron(II) gives rise, in octahedral complexes, to two different electronic ground terms, *viz.* high-spin $^5T_2(t_2{}^4e^2)$ as in $[Fe(H_2O)_6]^{2+}$ and low-spin $^1A_1(t^6{}_2)$ as in $[Fe(CN)_6]^{4-}$. The change between these two ground states should occur, according to ligand field theory, at a specific value of the cubic ligand field parameter Δ, equal to the spin-pairing energy π, where $\pi = \frac{5}{2}B+4C$, B and C being the electron repulsion parameters (Racah parameters). Thus $\Delta < \pi$ for $^5T_2$ and $\Delta > \pi$ for $^1A_1$ ground states.

If Δ is close to π, the separation between the two terms of different multiplicity may become comparable to the thermal energy kT. For relatively free molecules, a temperature dependent equilibrium between these terms ("spin-state equilibrium") is expected to occur. In the solid state, however, complications may arise, since the transfer of electrons between e and t_2 orbitals (arising in $^5T_2(t_2{}^4e^2) \rightleftharpoons {}^1A_1(t_2{}^6)$) should alter the ionic radius by a significant amount. The change of the electronic ground state may occur, therefore, by way of a cooperative ordering and thus a rather sharp transition in the various physical properties, *e.g.* the magnetic moment, might be expected.

In the free iron(II) ion, there exists, besides the ^5D ground term, both excited spin singlet and spin triplet terms. However, in ligand fields of strict octahedral symmetry, a term with two unpaired electrons ($S = 1$) cannot become the ground term[24]. Inspection of the Tanabe-Sugano diagram for the d^6 configuration[25] shows that in the neighborhood of the cross-over point the lowest triplet term $^3T_1(t_2{}^5e)$ is only a few kK above the ground state. In addition, there is extensive intermixing of the $^3T_1$, $^3T_2$, and $^5T_2$ terms via spin-orbit coupling. It is thus conceivable that a term consisting mainly of spin triplets may become the ground state in those complexes where $\Delta \sim \pi$.

A large part of the work reviewed here has been aimed primarily at clarification of the change from the high-spin to the low-spin ground states and at the determination of conditions under which states of intermediate (S = 1) spin are stabilized. To this end, the results of the various spectroscopic and magnetic investigations have been of particular value.

(i) Magnetic susceptibilities

The results of magnetic susceptibility measurements have been compiled in Table 2 in terms of the magnetic moment μ_{eff} at room temperature and the applicability of the Curie–Weiss law, $\chi_m = C_m/(T-\Theta)$. Here, χ_m is the molar magnetic susceptibility, C_m the Curie constant, T the temperature in °K, and Θ the Weiss constant. High-spin compounds within the series [Fe phen$_2$X$_2$] are represented by the ligands X = I, Br, Cl, N$_3$, NCO, HCOO, CH$_3$COO. At 293 °K, the moment values vary between 5.07 and 5.34 BM. These values are in agreement with μ_{eff} in excess of 4.90 BM as generally expected for $^5T_2$ ground states. The temperature dependence between 77 and 440 °K may be characterized empirically by a single Θ-value varying, for different compounds, between $-10°$ and $+9°$. Between 195 and 440 °K, the experimental results may be well approximated by the theory of paramagnetism for axially distorted $^5T_2$ ground terms[26,38]. In a field of axial symmetry, the $^5T_2$ term is split into a ^5E term and an orbitally non-degenerate term ($^5B_2$ in tetragonal, $^5A_1$ in trigonal fields), the energy separation Δ_{axial} being positive whenever ^5E is lowest. Taking the parameters of spin-orbit coupling and of orbital reduction as $\lambda = -80$ cm^{-1} and $\kappa = 0.8$ respectively, it has been shown[26] that the magnetic data fix Δ_{axial} between -700 cm^{-1} and -1440 cm^{-1} for [Fe phen$_2$X$_2$] complexes with X = Cl, Br, NCO, and N$_3$. If X = HCOO, the data can be fitted equally well with either $\Delta_{\text{axial}} = -560$ or $+2000$ cm^{-1}. Between 77 and 195 °K, deviations from the theoretically predicted curves are observed[26,27]. Rhombic field splittings of d electron levels have been suggested[26] as possible origins of these discrepancies.

Low-spin compounds within the series [Fe phen$_2$X$_2$] are represented by ligands providing relatively strong fields, *viz.* X = ½phen, NO$_2$, CNO, CN. At 293 °K, the molar susceptibilities have been determined as, *e.g.*, $\chi_m = -224$ for [Fe phen$_2$(CNO)$_2$][11] and $\chi_m = -107$ for [Fe phen$_2$(CN)$_2$]. 2H$_2$O[10] (other authors[17] reported $\chi_m = -60$), whereas from Pascal's constants, one calculates $\chi_m = -265$ and $\chi_m = -295$ respectively (all values in 10^{-6} cm^{3}mole^{-1}). Also, the susceptibilities were found to be reasonably constant[11,17,23] between 77 and

TABLE 2

MAGNETIC PROPERTIES OF [Fe phen$_2$X$_2$] AND RELATED COMPOUNDS

Compound	μ_{eff} *(BM) at 293 °K*	*Curie-Weiss law*[a]		*Ground State*[b]	*References*[c]
		T range (°K)	*Θ (°K)*		
[Fe phen$_2$I$_2$]	5.13	111–294	− 8	$^5T_2$	27
[Fe phen$_2$Br$_2$]	5.24	77–440	− 8	$^5T_2$	26, 9, 16, 27
[Fe phen$_2$Cl$_2$]	5.18	77–440	−10	$^5T_2$	26, 9, 16, 27
[Fe phen$_2$(N$_3$)$_2$]	5.20	77–440	0	$^5T_2$	26, 9, 16, 27
[Fe phen$_2$(NCO)$_2$]	5.07	77–440	− 9	$^5T_2$	26, 9, 16
[Fe phen$_2$(HCOO)$_2$]	5.27	77–440	+ 9	$^5T_2$	26, 9, 16
[Fe phen$_2$(CH$_3$COO)$_2$]	5.34			$^5T_2$	16
[Fe phen$_2$F$_2$] · 4H$_2$O	4.78	77–336	−15	$^3T_1$	28
[Fe phen$_2$ox] · 5H$_2$O	3.98	77–300	−20	$^3T_1$	28, 29
[Fe phen$_2$mal] · 7H$_2$O	3.80	77–300	−12	$^3T_1$	28, 29
[Fe phen$_2$(NCS)$_2$], (I)	5.17[d]			$^5T_2-{}^1A_1$	30, 31, 27
(II)	5.07[e]			$^5T_2-{}^1A_1$	30, 31
[Fe phen$_2$(NCSe)$_2$], (I)	4.98[f]			$^5T_2-{}^1A_1$	30, 31, 27
(II)	4.94[g]			$^5T_2-{}^1A_1$	30, 31
[Fe phen$_3$]$^{2+}$	~1.0			$^1A_1$	32, 33, 34
[Fe phen$_2$(NO$_2$)$_2$]	0.98			$^1A_1$	23, 35
[Fe phen$_2$(CNO)$_2$]	0.31			$^1A_1$	11
[Fe phen$_2$(CN)$_2$] · 2H$_2$O	0.68			$^1A_1$	10, 17, 9
[Fe dip$_2$Cl$_2$]	5.17			$^5T_2$	18
[Fe dip$_2$ox] · 3H$_2$O	3.90	77–293	−13	$^3T_1$	28
[Fe dip$_2$mal] · 3H$_2$O	3.90	77–293	− 9	$^3T_1$	28
[Fe dip$_2$(NCS)$_2$], (I)	5.23[h]			$^5T_2-{}^1A_1$	36, 27
(II)	5.21[i]			$^5T_2-{}^1A_1$	36
(III)	5.17[j]			$^5T_2-{}^1A_1$	36
[Fe dip$_3$]$^{2+}$	~1.0			$^1A_1$	37, 33
[Fe dip$_2$(CN)$_2$] · 3H$_2$O	0.61			$^1A_1$	10
[Fe dmph$_2$ox] · 4H$_2$O	4.11		−51	$^3T_1$	28
[Fe dmph$_2$mal] · 7H$_2$O	4.18		−19	$^3T_1$	28

[a] The Curie–Weiss law is used in the form $\chi_m = C_m/(T-\Theta)$.

[b] For convenience, the notation of octahedral symmetry is used.

[c] The reference, from which data were taken primarily, is listed first.

[d] At 77 °K, $\mu_{eff} = 0.65$ BM; transition temperature $T_c = 174$ °K.

[e] At 77 °K, $\mu_{eff} = 2.38$ BM; $T_c = 174$ °K.

[f] At 77 °K, $\mu_{eff} = 0.84$ BM; $T_c = 232$ °K.

[g] At 77 °K, $\mu_{eff} = 1.65$ BM; $T_c = 232$ °K.

[h] At 77 °K, $\mu_{eff} = 0.94$ BM; $T_c = 216$ °K.

[i] At 77 °K, $\mu_{eff} = 1.39$ BM; $T_c = 216$ °K.

[j] At 77 °K, $\mu_{eff} = 1.61$ BM; $T_c = 210$ °K.

293 °K. Therefore, these compounds are considered to have the diamagnetic ground term $^1A_1$, the small paramagnetic moment being due to temperature-independent paramagnetism.

The compounds [Fe phen$_2$(NCS)$_2$] (A), [Fe phen$_2$(NCSe)$_2$] (B), and [Fe dip$_2$(NCS)$_2$] (C) display a complicated temperature dependence of the magnetic moment. At 293 °K and above, μ_{eff} assumes values between 4.94 and 5.23 BM, decreases suddenly at a transition temperature T_c (T_c = 174 °K for A, T_c = 232 °K for B, and T_c = 215 °K for C), and approaches values between 0.65 and 2.38 BM at the lowest temperature investigated, *i.e.* 77 °K. In addition, the magnetic behaviour of compounds A and B is complicated by the existence of two polymorphs[30] (*viz.* I, II in Table 2) and that of compound C by the existence of three polymorphs[36] (*viz.* I, II, III). The respective polymorphs of one compound show virtually the same μ_{eff} values at 293 °K or, more generally, above T_c, whereas their magnetic moments differ strikingly below T_c and, particularly, at 77 °K. It is not clear at present whether the unique results of similar measurements by Baker and Bobonich[27] are due to their preparation of further polymorphs of these substances.

On the basis of Mössbauer effect and electronic spectral investigations (*vide infra*), it has been shown conclusively[30,36] that the sharp decrease of the magnetic moment at T_c involves a reversible transition between spin quintet and spin singlet electronic ground states (*viz.* $^5T_2$ and $^1A_1$ in O_h symmetry). The sharp nature of the magnetic change indicates that the transition does not originate wholly in a temperature dependent Boltzmann distribution over close-lying levels of the two multiplicities, but that, in addition, a co-operative effect might be involved.

The different values of μ_{eff} at 77 °K for each of the polymorphs have been associated with a varying percentage of complex molecules undergoing the transition $^5T_2 \rightarrow {}^1A_1$ (if T_c is approached from higher temperatures)[36]. Thus in each of the complexes studied, there is one polymorph (*viz.* polymorph I in A, B, C) where μ_{eff} is less than 1.0 BM (*i.e.* 0.65 BM for AI, 0.84 BM for BI, and 0.94 BM for CI). Assuming that this low temperature limiting value of μ_{eff} is due to temperature independent paramagnetism, the transition proceeds almost completely to $^1A_1$ in this polymorph. In all other polymorphs, the transition is incomplete.

Ground states of intermediate spin (*i.e.* $S = 1$) are encountered within the series [Fe phen_2X_2] in compounds where X_2 stands for bidentate oxalate (ox) or malonate (mal). At 293 °K, the magnetic moments of the solid complexes are 3.98 and 3.80 BM respectively. In 0.05M methanolic solution, μ_{eff} values of 3.80 and 3.82 BM (±0.15 BM) were obtained. The moments thus correspond to two unpaired electrons with a contribution ~1.0 BM from the second order Zeeman effect. The good agreement between the values from solids and solutions rules out the possibility that the intermediate μ_{eff} values could arise from intermolecular exchange interactions. Between 77 and 300 °K, the susceptibilities follow the Curie–Weiss law with $\Theta = -20$ and $-12°$ respectively. This fact as well as other results to be reported below have been used in a discussion[28] to exclude various alternative explanations for the observed moment values. Similar properties are encountered with the oxalate and malonate complexes of the dipyridyl and dimethylphenanthroline series (*cf.* Table 2). In addition, [Fe phen_2F_2] · $4H_2O$ also appears to have a spin-triplet ground state.

(ii) Mössbauer effect

Essentially two parameters are obtained from Mössbauer spectra: (i) the issomer hift δ is determined by the displacement of the center of the spectrum from zero; (ii) the quadrupole splitting ΔE_Q is defined by the magnitude of the separation of an absorption line into a doublet. Magnetic hyperfine splittings are not expected in the present compounds due to the relatively low concentration of iron.

The isomer shift measures the difference between the total s-electron densities at the nuclei of source and absorber according to[39]

$$\delta = \tfrac{2}{5}\pi Ze^2[R_{ex}^2 - R_{gr}^2]\,\{|\,\psi_s(O)\,|_a^2 - |\,\psi_s(O)\,|_s^2\}\,. \tag{3}$$

In (3), R_{ex} and R_{gr} are the effective radii of the nuclear excited and ground states of the 14.4 keV γ-transition in ^{57}Fe, respectively. In iron(II) compounds δ is in general larger for $^5T_2$ than for $^1A_1$ ground states[40]. This fact has been interpreted in terms of increased covalency of the metal–ligand bond in the $^1A_1$ state, since a larger d-electron delocalization is expected to decrease the shielding of core s electrons.

The quadrupole splitting ΔE_Q is caused by the interaction of the nuclear quadrupole moment Q with an electric field gradient (efg) in the region of the nucleus[41],

$$\Delta E_Q = \tfrac{1}{2}e^2 qQ(1+\tfrac{1}{3}\eta^2)^{\frac{1}{2}} \tag{4}$$

where $eq = V_{zz}$ and $\eta = (V_{xx} - V_{yy})/V_{zz}$, V being the electric potential. Since, in general, the largest contribution to the efg comes from incompletely-filled d electron shells, rather small values of ΔE_Q will be expected for the term $^1A_1(t_2{}^6)$. On the other hand, substantial values of ΔE_Q should result from $^5T_2(t_2{}^4e^2)$ terms in the absence of octahedral symmetry. These expectations are well supported by the available experimental data[40].

In Table 3 the results of ^{57}Fe Mössbauer effect investigations on the compounds dealt with here are given. Only the normal temperature shift has been observed between 293 and 77 °K with all the complexes[42] entered under (i), (ii), and (iv). Therefore, the data obtained at 77 °K are listed for one example in each group only. Some of the high-spin compounds have been measured at room temperature by Duncan and Mok[43] and the results used in a theoretical analysis by Golding *et al.*[44] These authors reported values of δ relative to a stainless steel source which requires *subtraction* of 0.10 mm/sec to convert to natural iron. The agreement of the corrected isomer shift data with the more detailed results of König, Hüfner, Steichele, and Madeja[42] is reasonable, that of the quadrupole splittings is less satisfactory. The discrepancy is probably caused by the larger experimental uncertainties involved in the data of the previous authors[43,44]. This affects also, for the present compounds, the correlations between values of ΔE_Q and μ_{eff} discussed by Golding *et al.*[44] Finally, the data reported by Collins, Pettit, and Baker[47], as derived from Mössbauer effect measurements on a number of the present compounds at 77 °K, are in error. On careful reinvestigation, these authors[48] were able to confirm the results of König *et al.*[42]

As expected, both the values of δ and ΔE_Q are much larger for [Fe phen$_2$X$_2$] compounds in $^5T_2$ than in $^1A_1$ ground states. The isomer shifts of the high-spin compounds have been used to determine the 4s-character x in the configuration $(3d)^6(4s)^x$ on the basis of eq. (3) and employing an improved diagram similar to that of Walker *et al.*[39] Disregarding d electron bonding effects one obtains values[42] between x = 0.19 and x = 0.27. However, these results have to be considered with reservation, since a correlation between isomer shift δ and nephelauxetic effect has been established[42]. The temperature dependence of ΔE_Q in high-spin [Fe phen$_2$X$_2$] complexes has been used to estimate the axial field splitting Δ_{axial} of the $^5T_2$ ground term. The Δ_{axial} values obtained are in reasonable agreement with those deduced from the magnetic susceptibilities[26].

Comparison of δ and ΔE_Q values determined for the compounds [Fe phen$_2$(NCS)$_2$], [Fe phen$_2$(NCSe)$_2$], and [Fe dip$_2$(NCS)$_2$] with those listed in Table 3 under (i) and (ii) provides conclusive evidence for the existence of these compounds in a $^5T_2$ ground state at 293 °K and in a $^1A_1$ ground state at 77 °K. This inference holds equally well for all the polymorphs studied. The change between the Mössbauer spectra characteristic of the two ground states of different multiplicity occurs at the same transition temperature T_c which was observed in the magnetic susceptibilities. Starting from higher and proceeding to lower temperatures, both Mössbauer spectra co-exist in the region of the sharp decrease of the magnetic moment (approx. 5 to 15° about T_c[30,36]), that typical of the $^5T_2$ state with decreasing, that typical of the $^1A_1$ state with increasing intensity[49,50]. The fact that separate Mössbauer transitions for the high-spin and low-spin states can be observed requires thermal relaxation times for the change from one state to the other to be long relative to the lifetime of the ^{57}Fe $I = \frac{3}{2}$ nuclear excited state ($\tau = 1.45 \times 10^{-7}$ sec). The statement of Jesson *et al.*[53,76] that, in the present compounds, separate Mössbauer transitions are not observed, is incorrect.

If the transition between $^5T_2$ and $^1A_1$ ground states is governed by a temperature dependent Boltzmann distribution over close-lying levels of multiplicities five and one alone ("spin-state equilibrium"), a single average efg, which would depend on the contribution of each level to the equilibrium, would be expected. The relaxation time for the transition would thus be shorter than the lifetime of the $I = \frac{3}{2}$ state of the ^{57}Fe nucleus. This situation has, in fact, been encountered in some *tris*(*N*,*N*-dialkyldithiocarbamates) of iron(III)[51], where $^6A_1$ and $^2T_2$ states are involved in the equilibrium[52]. In the present compounds, where this is not observed, it seems more appropriate to speak of a $^5T_2-{}^1A_1$ transition[36] rather than of a $^5T_2-{}^1A_1$ equilibrium as initiated previously[30]. Moreover, the present situation seems to be more common[53] than that of a spin-state equilibrium with a relaxation time $T_R < 1.45 \times 10^{-7}$ sec.

The results listed in Table 3 under (iv) differ conspicuously from the data tabulated under (i), (ii), and (iii). There seems to be only one other iron(II) compound studied by Mössbauer spectroscopy *viz.* iron(II) phthalocyanine[54], $\delta =$

TABLE 3

^{57}Fe MÖSSBAUER EFFECT RESULTS ON [Fe $phen_2X_2$] AND RELATED COMPOUNDS

Compound	*T* (°K)	$\delta^{a,b}$ (*mm/sec*)	$\Delta E_Q{}^a$ (*mm/sec*)	*References*[c]
(i) high-spin $^5T_2$:				
[Fe $phen_2Cl_2$]	293	+0.96	3.00	42, 43, 44
	77	+0.98	3.27	42
[Fe $phen_2Br_2$]	293	+1.05	2.94	42, 43, 44
[Fe $phen_2(N_3)_2$]	293	+0.99	2.79	42
[Fe $phen_2(OCN)_2$]	293	+1.06	2.86	42, 43
[Fe $phen_2(HCOO)_2$]	293	+1.06	2.40	42, 43
[Fe $phen_2(CH_3COO)_2$]	293	+1.09	2.68	42
[Fe dip_2Cl_2]	293	+1.01	3.04	42
(ii) low-spin $^1A_1$:				
[Fe $phen_3$] $(ClO_4)_2$[d]	room	+0.25	0.00	46, 45
[Fe $phen_2(NO_2)_2$]	293	+0.28	0.38	42
	77	+0.25	0.41	42
[Fe $phen_2(CN)_2$] · $2H_2O$	room	−0.03	0.60	46
[Fe $phen_2(CN)_2$] · H_2O	293	+0.20	0.59	42
[Fe dip_3] $(ClO_4)_2$	room	+0.30		45
[Fe $dip_2(CN)_2$] · $2H_2O$	room	+0.12	0.65	46
(iii) transition $^5T_2$-$^1A_1$:				
[Fe $phen_2(NCS)_2$][e]	293	+0.98	2.67	30, 31, 42
	77	+0.37	0.34	30, 31, 42
[Fe $phen_2(NCSe)_2$][e]	293	+1.01	2.47	30, 42
	77	+0.40	0.18	30, 42
[Fe $dip_2(NCS)_2$][e]	293	+1.06	2.18	36, 42
	77	+0.36	0.50	36, 42
(iv) intermediate spin $^3T_1$:				
[Fe $phen_2$ox] · $5H_2O$	293	+0.33	0.21	42
[Fe $phen_2$mal] · $7H_2O$	293	+0.34	0.18	42
	77	+0.27	0.18	42
[Fe $phen_2F_2$] · $4H_2O$	293	+0.33	0.21	42
[Fe dip_2ox] · $3H_2O$	293	+0.34	0.26	42
[Fe dip_2mal] · $3H_2O$	293	+0.30	0.31	42
[Fe $dmph_2$ox] · $4H_2O$	293	+0.36	0.23	42
[Fe $dmph_2$mal] · $7H_2O$	293	+0.33	0.27	42

[a] Experimental uncertainty in general less than ±0.05 mm/sec.

[b] Isomer shifts δ are listed relative to the center of the spectrum of a natural iron absorber at 293 °K. Movement of the source towards the absorber corresponds to positive velocities.

[c] The reference, from which data were taken primarily, is listed first.

[d] For data on the same complex ion with various other anions, *cf.* reference 43.

[e] Virtually identical data were obtained for all polymorphs of the compound.

0.40 mm/sec (*cf.* footnote b in Table 3), which shows a comparable value of the isomer shift. Since this compound is considered to have a triplet ground state[55], independent support is provided for a component of $^3T_1$ as lowest state in the compounds listed. Complexes with *trans* arrangement of ligands show, in general, a much more pronounced variation in ΔE_Q, *cf.*, for example, tetrapyridinecomplexes of iron(II)[44] and the phthalocyanine iron(II) dipyridine, di(γ-picoline), and diimidazole adducts[56] for iron(II) compounds in quintet and singlet ground states, respectively. Complexes with ligands in *cis* position usually exhibit only a slight variation in ΔE_Q, *cf.* the [Fe phen$_2$X$_2$] compounds listed under (i) and (ii). Thus Mössbauer results suggest that the complexes tabulated as (iv) should be of *cis* configuration. Since these compounds involve three bidentate ligands, it is very likely that they are of monomolecular structure.

(iii) Infrared spectroscopy

Infrared spectroscopic studies may yield valuable information with respect to both molecular structure and bonding properties in the compounds considered. Thus the molecular symmetry of [Fe (diamine)$_2$X$_2$] compounds may often be inferred from a study of the vibrational frequencies pertaining to the ligands X. In addition, the diamine parts of the spectra may be useful concerning certain aspects of the electronic structure.

The infrared frequencies characteristic of the ligands X are listed in Table 4. In several instances, these data have been used to support a *cis* arrangement of the complexes. Thus a splitting of the CN stretching frequency by 13 cm^{-1} has been observed by Schilt[58] and was taken as evidence for the *cis* structure of [Fe phen$_2$(CN)$_2$] · 2H$_2$O. An analogous splitting of the CN stretching mode is encountered in spectra from both the $^5T_2$ and $^1A_1$ ground states of [Fe phen$_2$(NCS)$_2$], [Fe phen$_2$(NCSe)$_2$], and [Fe dip$_2$(NCS)$_2$][30,36] as well as in [Fe phen$_2$(NCO)$_2$] (*cf.* Table 4). These compounds have therefore to be considered as *cis*.

TABLE 4

INFRARED FREQUENCIES OF LIGANDS X IN [Fe phen$_2$X$_2$] AND RELATED COMPOUNDS

Compounds	*Assignment and wavenumber (cm^{-1})*[a]	*Reference*
[Fe phen$_2$Cl$_2$]	ν_{as}(Fe–Cl) = 257 (s)	57
[Fe dip$_2$Cl$_2$]	ν_{as}(Fe–Cl) = 246 (s); ν_s(Fe–Cl) = 230 (s)	57
[Fe phen$_2$(N$_3$)$_2$]	ν_1 = 1323 (m); ν_2 = 611 (m); ν_3 = 2038 (vs)	57
[Fe phen$_2$(NCO)$_2$]	ν_1 = 2203 (vs), 2188 (vs); ν_2 = 626 (s), 616 (s); ν_3 = 1318 (s)	57
[Fe phen$_2$(HCOO)$_2$]	ν_{as}(CH) = 2792 (s); ν_s(CH) = 2712 (s), 2695 (s); ν_{as}(COO) = 1626 (vs), 1607 (vs); ν_s(COO) = 1312 (s, br); π(COO) or π(CH) = 955 (s); δ(OCO) = 770 (vs)	57
[Fe phen$_2$(CH$_3$COO)$_2$]	ν_{as}(COO) = 1595 (vs, br), 1555 (vs, sh);, ν_s(COO) = 1386 (vs); δ(CH$_3$) = 1445 (s); ρ_r(CH$_3$) = 1034 (m); ρ_r(CH$_3$) = 1000 (s), 990 (s); ν(CC) = 944(s), 912(s); δ(OCO) = 638 (vs); π(COO) or π(CH) = 612 (s), 604 (m); ρ_r(COO) or δ(CH) = 483	57
[Fe phen$_2$(CN)$_2$] · 2H$_2$O	ν(CN) = 2075 (vs), 2062 (vs)	58
[Fe phen$_2$(CN)$_2$] · H$_2$O	ν(CN) = 2076 (vs), 2063 (vs)	57
[Fe phen$_2$(CNO)$_2$] · H$_2$O	ν_1 = 2119 (m); ν_3 = 1101 (vs), 1085 (vs)	11
[Fe dip$_2$(CNO)$_2$] · $\frac{1}{2}$H$_2$O	ν_1 = 2115 (m); ν_3 = 1113 (s), 1089 (vs)	11
[Fe phen$_2$(NO$_2$)$_2$]	ν_{as}(NO$_2$) = 1366 (vs), 1336 (vs); ν_s(NO$_2$) = 1282 (vs), 1313 (vs), 1346 (s); δ(ONO) = 820 (s), 813 (s), 803 (w); ρ_w(NO$_2$) = 610 (m)	57

TABLE 4 (continued)

Compounds	*Assignment and wavenumber* (cm^{-1})[a]	*Reference*
[Fe $phen_2(NCS)_2$], $^5T_2$	ν_1 = 2075 (vs), 2063 (vs); ν_2 = 483 (s), 473 (s); ν_3 = 809 (w)	30
$^1A_1$	ν_1 = 2116 (vs), 2108 (vs); ν_2 = 476 (s); ν_3 = 809 (vs), 807 (vs)	30
[Fe $phen_2(NCSe)_2$], $^5T_2$	ν_1 = 2075 (vs), 2065 (vs);	30
$^1A_1$	ν_1 = 2112 (vs), 2106 (vs);	30
[Fe $dip_2(NCS)_2$], $^5T_2$	ν_1 = 2065 (vs), 2055 (vs); ν_2 = 477 (m), 473 (w, sh); ν_3 = 802 (m)	36
$^1A_1$	ν_1 = 2118 (vs), 2109 (vs); ν_2 = 475 (m), 470 (m); ν_3 = 804 (vs), 798 (s)	36
[Fe $phen_2ox$] · $5H_2O$	ν_7 = 1707 (s); ν_1 = 1660 (vs, br); ν_2 = 1363 (vs, br); ν_8 = 1260 (sh), 1252 (s, br); ν_3 = 887 (m, br); ν_9 = 789 (vs), 778 (sh); ν_4 = 523 (s); ν_{10} = 484 (m, br); ν_{11} = 337 (vs, br); ν_5 = 321 (sh)	28, 29
[Fe dip_2ox] · $3H_2O$	ν_7 = 1706 (s); ν_1 = 1660 (vs, br); ν_2 = 1365 (vs, br) ν_8 = 1265 (sh), 1250 (s, br); ν_3 = 888 (s, br); ν_9 = 789 (vs); ν_4 = 522 (s); ν_{10} = 482 (s, br); ν_{11} = 340 (vs, br); ν_5 = 323 (sh)	28
[Fe $dmph_2ox$] · $4H_2O$	ν_7 = 1706 (s); ν_1 = 1660 (vs, br); ν_2 = 1363 (vs, br); ν_8 = 1258 (s, br); ν_3 = 885 (m, br); ν_9 = 789 (vs), 780 (sh); ν_4 = 522 (s); ν_{10} = 479 (s); ν_{11} = 338 (vs, br); ν_5 = 320 (sh)	28
[Fe $phen_2mal$] · $7H_2O$	ν_{as}(CO) = 1610 (vs, br); CH_2 bend+ν_s(CO) = 1405 (sh); ν_s(CO) = 1373 (vs, br); CH_2 wagg = 1290 (m, br); ν_s(CC) = 957 (s); CH_2 rock = 928 (s); δ(OCO) = 778 (m, br); δ(OCO) = 710 (s); ν(Fe–O) = 550 (m, br); ν(Fe–O) = 347 (vs, br); δ(OCO) = 325 (s, sh)	28, 29
[Fe dip_2mal] · $3H_2O$	ν_{as}(CO) = 1610 (vs, br); CH_2 bend+ν_s(CO) = 1395 (sh); ν_s(CO) = 1375 (vs, br); CH_2 wagg = 1295 (m, br); ν_s(CC) = 958 (s); CH_2 rock = 927 (s); δ(OCO) = 780 (sh); δ(OCO) = 713 (s); ν(Fe–O) = 552 (m, br); ν(Fe–O) = 345 (vs, br); δ(OCO) = 325 (s, sh)	28
[Fe $dmph_2mal$] · $7H_2O$	ν_{as}(CO) = 1610 (vs, br); CH_2 bend+ν_s(CO) = 1395 (sh); ν_s(CO) = 1373 (vs, br); CH_2 wagg = 1290 (m, br); ν_s(CC) = 958 (s); CH_2 rock = 929 (s); δ(OCO) = 790 (sh); δ(OCO) = 714 (s); ν(Fe–O) = 555 (m, br)	28
[Fe $phen_2F_2$] · $4H_2O$	ν(Fe–F) = 525 (vs, sh), 495 (vs, br)	28

---

[a] The numbering of frequencies follows, in general, the usage of Ref. 59.

A splitting of the NO stretch in [Fe $phen_2(CNO)_2$] · H_2O and [Fe $dip_2(CNO)_2$] · $\frac{1}{2}H_2O$ has likewise been employed in support[11] of a *cis* configuration. In [Fe $phen_2(NO_2)_2$], a *cis* structure is very likely, since at least five well separated NO_2 stretching modes can be distinguished (*cf.* Table 4). There are definite similarities between the oxalate frequencies in [Fe $phen_2ox$] · $5H_2O$, [Fe dip_2ox] · $3H_2O$, and [Fe $dmph_2ox$] · $4H_2O$ and those in, for example, [$Cr(NH_3)_4ox$]Cl, particularly as far as the vibrational modes ν_4 at 522 cm^{-1} and ν_{11} at 340 cm^{-1} are concerned (predominantly Fe–O stretch)[28]. This correspondence again suggests a *cis* structure for the compounds in question. The same conclusion may be drawn for the analogous malonate complexes[28]. In addition, the splittings of Fe-halogen stretches which are observed in [Fe $phen_2F_2$] · $4H_2O$ and in [Fe dip_2Cl_2] (*cf.* Table 4) are indicative of a *cis* arrangement. Summing up, there is strong infrared evidence for a *cis* molecular structure of most [Fe $(diamine)_2X_2$] complexes known at present. This preference for a *cis* arrangement is not surprising at least for the bis(phenanthroline) compounds, since two phenanthroline molecules cannot be accomodated in the same plane without nonbonded H–H interactions in the 2,9 position[60].

There is no indication of Fe–N(diamine) stretching vibrations within the range studied. A recently proposed assignment[43] of two bands at 525 and 290 cm^{-1} to iron–nitrogen vibrations is considered very unlikely on the basis of mass considerations as applied to metal–ammonia vibrations[59]. Also, metal–pyridine vibrations have been convincingly assigned[61,62] between 200 and about 250 cm^{-1}. Thus Fe–N(dip) and Fe–N(phen) stretching vibrations are not expected to occur above 200 cm^{-1}; at least in the high-spin compounds considered here. In the $^1A_1$ ground states of [Fe $phen_2(NCS)_2$] and [Fe $phen_2(NCSe)_2$], two bands have been observed at 375/367 and 368/360 cm^{-1}, respectively[63], which are not encountered in the $^5T_2$ states of the complexes. It is not unlikely that these bands are in fact due to Fe–N(phen) stretching vibrations which might have been shifted to higher energy by the increased interaction of iron(II) and the phenanthroline ligands. The problem is being investigated by extending the infrared spectra to lower frequencies.

From the position of the frequencies ν_1, ν_2, and ν_3 it is concluded that, in the present compounds, the ligands NCO, NCS, and NCSe are coordinated to the metal atom through nitrogen. Arguments have been put forward[30,36] which show that in [Fe $phen_2(NCS)_2$], [Fe $phen_2(NCSe)_2$], and [Fe $dip_2(NCS)_2$] this is true for both the $^5T_2$ and $^1A_1$ ground states. The shift of the CN stretching mode by $\sim$50 cm^{-1} to higher frequencies on transition from the $^5T_2$ to the $^1A_1$ ground state is taken as evidence of the smaller size of the iron(II) ion in the $^1A_1$ ground state and of the increased back donation of t_2 electrons to the diamine ligands. Since these effects give rise to a larger ionic interaction with the NCS and NCSe ligands, the observed band shift results. These arguments are consistent with a recent X-ray structure investigation (*vide infra*).

The different position of the characteristic double band, corresponding to the CN stretching mode in the isothiocyanato and isoselenocyanato complexes, is a valuable "fingerprint" of the molecules present in $^5T_2$ and $^1A_1$ ground states. This band has been used, therefore, to investigate the reason for the different magnetic moments observed in the various polymorphs of these substances[36] below T_c. Thus, in the polymorphs having μ_{eff} less than 1.0 BM at 77 °K (*cf.* Table 2), only $\nu_1(^1A_1)$ is observed at this temperature. The other polymorphs (*i.e.* AII, BII, CII, and CIII, *cf.* p. 477 for the notation used) exhibit at 77 °K both $\nu_1(^1A_1)$ and $\nu_1(^5T_2)$, the latter with higher intensity the higher the magnetic moment. These results demonstrate that the higher μ_{eff} values of these polymorphs originate in some percentage of molecules which remain in the $^5T_2$ ground state even below T_c.

As far as the diamine ligands are concerned, characteristic differences have been established[63] between the infrared spectra of [Fe (diamine)$_2$X$_2$] compounds in $^5T_2$ and those in $^1A_1$ ground states. The most significant of these seems to be present in the region of the CC and CN stretching vibrations. Thus, in the phenanthroline complexes, for example, there are very strong bands at 1515 and 1495 cm^{-1} in the $^5T_2$ ground state. These become extremely weak in the $^1A_1$ state. This observation has been explained by assuming a π electron distribution on phenanthroline which is virtually unchanged from that of the free ligand in the $^5T_2$ state while in the $^1A_1$ state the conjugation of π electrons on the ligand seems to be greatly diminished. In addition, splittings of various bands indicate a considerably lower ligand symmetry in the $^1A_1$ ground state. The numerous differences which have been listed and discussed[36,63] may be rationalized in terms of increased double-bond character of the Fe–N(diamine) bonds in the $^1A_1$ ground state.

The infrared frequencies of diamine ligands in [Fe(diamine)$_2$X$_2$] compounds with a triplet ground state correspond closely to those of the analogous compounds in $^1A_1$ states. It has been suggested[28] that nearly identical metal-diamine ligand distances and bonding should be expected.

(iv) Electronic spectroscopy

The d-d bands in the electronic spectra of [Fe(diamine)$_2$X$_2$] complexes vary according to the different electronic ground states. Thus compounds in $^5T_2$ ground states (in the approximation of O_h symmetry) generally show two resolved bands within the region[9] 8500 to 12,500 cm^{-1}. Since all of these compounds very likely have a *cis* molecular structure (*cf.* section (iii)), the two bands in the near infrared would correspond to the transition $^5E \leftarrow {}^5T_2$, the excited ^5E state being split in C_2 symmetry into $^5A + {}^5B$ with a separation of about 2000 cm^{-1}. The energies of the bands have been discussed in terms of the σ and π antibonding effects of the ligands and the angular overlap model[65]. Their separation has been used in support of ground state splittings of comparable magnitude[44], but there is no simple relation between ground and excited state splittings in C_2 symmetry[65].

In single crystals of [Fe dip$_3$]Br$_2$ · 6H$_2$O, the single observed d–d band at 11,500 cm^{-1} ($\varepsilon = 4.2$) has been assigned[66] on the basis of its width, intensity, and polarization to the $^3T_1 \leftarrow {}^1A_1$ transition substantially mixed with the charge-transfer band at ~18,800 cm^{-1}. In the ion [Fe phen$_3$]$^{2+}$ in solution, a similar band has been observed[67] at 12,260 cm^{-1} ($\varepsilon = 4.4$) and should be assigned analogously. The previously suggested assignment[67] is in disagreement with recent experimental findings[66]. In [Fe phen$_2$(CN)$_2$], a weak shoulder which again might be due to the $^3T_1 \leftarrow {}^1A_1$ transition has been observed at ~12,500 cm^{-1}.

The spectrum of [Fe phen$_2$(NCS)$_2$] has been studied at 298 and ~77 °K, *i.e.* in both the $^5T_2$ and $^1A_1$ ground states[30]. The $^5E \leftarrow {}^5T_2$ transition occurs at 11,900 cm^{-1}, and the weak band found at ~10,400 cm^{-1} in the 77 °K spectrum has been assigned to the transition $^3T_1 \leftarrow {}^1A_1$. Virtually identical spectra[30] have been obtained for [Fe phen$_2$(NCSe)$_2$]. From these data, values of the spectral parameters have been estimated as $\Delta = 11{,}900$ cm^{-1} and B ~ 640 cm^{-1} for the $^5T_2$ ground state and $\Delta \sim 16{,}300$ cm^{-1} and B ~ 580 cm^{-1} for the $^1A_1$ ground state. The inequality

$$\Delta(^5T_2) < \pi < \Delta(^1A_1), \tag{5}$$

where π is the spin-pairing energy, thus appears to be satisfied in this case. The increase in Δ per electron transferred from an e to a t$_2$ orbital is ~18.5%. The decrease in the nephelauxetic parameter from $\beta(^5T_2) = 0.61$ to $\beta(^1A_1) = 0.55$ indicates increased back π bonding in the $^1A_1$ state, in agreement with deductions from Mössbauer effect and infrared spectral observations.

From the completely analogous spectra of the three polymorphs of [Fe dip$_2$-(NCS)$_2$][36] at room temperature, the parameter values $\Delta = 11{,}200$ cm^{-1} and B ~ 605 cm^{-1} characteristic of the $^5T_2$ ground state have been obtained. Unfortunately, the 77 °K spectra have not been well resolved.

The d-d spectra of [Fe(diamine)$_2$X$_2$] complexes which are supposed to exist in a triplet ground state show a band of weak intensity in the 12,000 cm^{-1} region. The assignment of this band is uncertain.

All the [Fe (diamine)$_2$X$_2$] complexes reviewed here exhibit an intense charge-transfer band in the visible region of the spectrum. Williams[68] has shown by a comparative study of various substituted phenanthrolines that the band in the spectrum of the [Fe phen$_3$]$^{2+}$ ion is caused by inverted electron transfer from iron(II) to antibonding ligand orbitals. Recently, Day and Sanders[69,70] have demonstrated that the electron is transferred into the next to lowest empty orbital, π^{**}, and thus the transition may be written as (core)π^2t$_2{}^6$ → (core)π^2t$_2{}^5\pi^{**}$. In the dipyridyl complexes, the assignment of the bands to a charge-transfer transition is supported by single crystal studies[66] on [Fe dip$_3$]Br$_2$ · 6H$_2$O. Two factors are significant in this regard: the narrow half-width of the band and the temperature dependence of its intensity.

In the [Fe phen$_3$]$^{2+}$ ion, the charge-transfer band occurs at 19,600 cm^{-1} (main peak) with $\varepsilon = 11{,}100$. Substitution of methyl groups on the ligands shifts the band to lower or higher energies[69], the largest red-shift being observed with 5,6-dimethyl-1,10-phenanthroline ($\nu_{CT} = 19{,}230$ cm^{-1}) and the largest blue-shift with 3,8-dimethyl-1,10-phenanthroline ($\nu_{CT} = 20{,}160$ cm^{-1}). In [Fe phen$_2$X$_2$] complexes, shifts to lower energies are usually encountered. Thus in [Fe phen$_2$(CN)$_2$] with a $^1A_1$ ground state, the main peak is at 16,670 cm^{-1}. In [Fe phen$_2$Cl$_2$], *e.g.*, which has a $^5T_2$ ground state, the first (*i.e.* lowest energy) peak is found at 16,670 cm^{-1} again, whereas the second, more intense peak occurs at 18,700 cm^{-1}. In

[Fe $\text{phen}_2(\text{NCS})_2$], the ${}^5T_2 \rightarrow {}^1A_1$ transition is accompanied by a shift of the main peak in the charge-transfer band from 18,000 cm^{-1} to 17,200 cm^{-1} (the first peak shifts to 15,900 cm^{-1}). In [Fe phen_2ox] $\cdot$ $5\text{H}_2\text{O}$ with a triplet ground state, the first and most intense peak is situated at 18,850 cm^{-1}. It may be concluded that the multiplicities of the ground states, and thus electron repulsion effects, cause only minor variations to the energies of these inverted charge-transfer bands.

At energies higher than those of the charge-transfer band, internal $\pi \rightarrow \pi^*$ ligand transitions are observed. Compared to the corresponding transitions of the free ligands, these bands are usually shifted to lower energies due to the reverse crystal-field effect[71,71a].

(*v*) *Electron paramagnetic resonance*

Only limited paramagnetic resonance absorption studies on polycrystalline samples have been made. Thus in [Fe $\text{dip}_2(\text{NCS})_2$], polymorph III gives an intense resonance line at 293 °K with $g = 2.24$ and a half-width $\Delta H^1/_2 \sim 900$ Gauss[36]. The fact that the absorption intensity is virtually unaffected at 77 °K has been explained as due to a balance between the expected intensity increase (varying as $1/T$) and the decrease in the number of paramagnetic Fe^{2+} ions below T_c (corresponding to the lowering of μ_{eff} from 5.17 at 293 °K to 1.61 BM at 77 °K).

The compounds [$\text{Fe(diamine)}_2\text{X}_2$] with a triplet ground state exhibit two broad bands at $g \sim 2.1$ and $g \sim 4.1$ respectively[28]. A definite assignment is difficult due to the large line width (300 to 1500 Gauss). At present, measurements on solutions are being attempted[23].

(*vi*) *X-ray crystallographic structural studies*

From X-ray diffraction powder data, it was suggested by Baker and Bobonich[27] that complexes [Fe phen_2X_2], where X = Cl^-, Br^-, I^-, and N_3^-, belong to one structural class, while complexes having X = NCS^- and NCSe^- belong to another. This has been taken as evidence in support of a *cis* molecular structure for the first group and a bridged bimolecular structure for the second group. Although the first assumption seems to be reasonable on the basis of infrared data (*cf.* section (iii)), the second has been ruled out by the infrared spectral, magnetic susceptibility and Mössbauer effect observations[30]. Further, it is hardly surprising that the crystal structures (and hence the powder data) for mononuclear *cis* complexes with X = NCS^- and NCSe^- ligands should differ from the others when the large differences in ligand dimensions are considered.

Powder data of the compounds [Fe phen_2X_2] having X = NCS^- and NCSe^- have been studied both above and below[27,30] the transition temperature T_c. Since no differences could be detected, it was concluded that no first order crystallographic phase changes are involved in the magnetic transitions which take place[30] at T_c. This issue was subsequently challenged by Casey and Isaacs[77] and by Goodwin and Sylva[78]. However, on the basis of single crystal Weissenberg photographs of [Fe dip$_2$(NCS)$_2$] taken above and below T_c, König, Madeja, and Watson[36] have clearly shown that, at least in this compound, a phase change is not observed. Since the properties of both phenanthroline complexes which show $^5T_2 - {}^1A_1$ transitions, are closely related to those of [Fe dip$_2$(NCS)$_2$], we consider the possibility of a phase change in these complexes as not very likely.

Space groups and lattice parameters have been determined from single crystal diffraction data of three substances within the series [Fe(diamine)$_2$X$_2$] and are listed in Table 5. Full crystal structure analyses on [Fe dip$_2$(NCS)$_2$], polymorph II, at 293 °K and at ~100 °K are in the process of refinement. Preliminary results[72] show that the Fe-N(dip) bond length decreases from about 2.17 Å in the $^5T_2$ ground state to about 2.03 Å in the $^1A_1$ ground state. The difference of ~0.14 Å clearly reflects the change in radius of the iron(II) ion in going from the high-spin $t_2^4e^2$ to the low-spin t_2^6 configuration. Such a difference in radii has been predicted, on the basis of ligand field theory, as early[79] as 1952. However, to our knowledge, a confirmation by X-ray structure methods has never been presented. In the present context, the small Fe–N(dip) distance accounts for the strong metal-ligand interaction in the $^1A_1$ state which was inferred from the results of various spectroscopic investigations. The Fe–N(NCS) bond length likewise becomes shorter *viz.* ~2.09 Å in the $^5T_2$, ~2.01 Å in the $^1A_1$ ground state. In agreement with nifrared results, there is no difference in the C–S distance. On the other hand, the C–N bond length changes from ~1.08 Å in the $^5T_2$ to ~1.16 Å in the $^1A_1$ ground state. It should be emphasized that these results may change somewhat, subject to further refinement. In addition, it has been established definitely that the NCS groups are N-bonded and *cis*.

TABLE V

UNIT CELL DATA OF [Fe(diamine)$_2$X$_2$] COMPOUNDS

Compound	*Space group*	*Lattice Parameters, Å*	*Molecules per unit cell*	*References*
[Fe dip$_2$(NCS)$_2$], polymorph I	orthorhombic, Pbca (= D_{2h}^{15})	$a = 16.04$ $b = 16.98$ $c = 15.94$	8	36
[Fe dip$_2$(NCS)$_2$], polymorph II	orthorhombic, Pcnb (= D_{2h}^{14})	$a = 13.17$ $b = 16.50$ $c = 10.08$	4	36
[Fe phen$_2$ox] · 5H$_2$O	triclinic, $P\bar{1}$ or $P1$	$a = 16.23$ $b = 63.2$ $c = 10.56$ $\alpha = 92°05'$ $\beta = 102°21'$ $\gamma = 90°40'$	16	28

D. RELATIONS BETWEEN MOLECULAR PARAMETERS, CRYSTAL LATTICE EFFECTS, AND MAGNETIC PROPERTIES NEAR THE $^5T_2-{}^1A_1$ CROSSOVER

In order to understand the magnetic and the various spectroscopic properties of [Fe(diamine)$_2$X$_2$] complexes, the changes in the spectroscopic parameters when varying X over the series of ligands (1) might be examined.

The electronic spectrum[9] of high-spin [Fe phen$_2$Cl$_2$] shows two bands ("$^5T_2$" → ^{5}A, "$^5T_2$ → ^{5}B of C_2 symmetry) of almost equal intensity at 8470 and 10,510 cm^{-1}. This results in an average value of Δ = 9490 cm^{-1}. The two bands of [Fe phen$_2$Br$_2$] yield analogously Δ = 9610 cm^{-1}. Proceeding further to the right in the spectrochemical series, [Fephen $_2$(NCO)$_2$] exhibits a slightly asymmetric band[9] which gives Δ = 11,350 cm^{-1}. The same is true[30] of [Fe phen$_2$(NCS)$_2$] and [Fe phen$_2$(NCSe)$_2$] at 293 °K, where $\Delta(^5T_2)$ = 11,900 cm^{-1}. Since, in these compounds, the transition between the ground states $^5T_2$ and $^1A_1$ has been observed on cooling to T_c = 174 °K and 232 °K respectively, the value of $\Delta(^5T_2)$ must be very close to the spin-pairing energy π. In fact, work on a wide variety of α-diimine complexes indicates[73] that, for Fe^{2+}, π = 12,500 ± 800 cm^{-1}. Below T_c, $\Delta(^1A_1) \sim$ 16,300 cm^{-1} has been estimated[30], showing the expected increase of ~20%. In the [Fe phen$_3$]$^{2+}$ ion, the value of Δ cannot be determined from the spectrum, since only the electronic transition $^3T_1 \leftarrow {}^1A_1$ has been observed[30,66,67]. Using the equation[74]

$$\Delta = (12.2-0.75\,q+0.4\,\varrho)10^3 \text{ cm}^{-1} \tag{6}$$

where ϱ is the ligand field stabilization parameter for the configuration 3d^q, Δ may be estimated[30] as ~18,000 cm^{-1}. This result and the value of 31,400 cm^{-1} for [Fe(CN)$_6$]$^{4-}$ [75] give Δ = 22,470 cm^{-1} for [Fe phen$_2$(CN)$_2$] at the right end of the spectrochemical series. The observed behaviour of [Fe phen$_2$X$_2$] compounds is thus in complete agreement with the variation of Δ throughout the series (1).

A necessary prerequisite for the stabilization of a spin-triplet ground state is that Δ_{triplet} should be confined to values between the high-spin and the low-spin limit for π, *i.e.* 11,900 < Δ_{triplet} < 16,300 in cm^{-1}. The reason is that, at $\Delta \sim \pi$, the $^3T_1$ term assumes its lowest energy above the ground state[28]. Since Δ for the oxalate and malonate ligands is practically equal to the value for H$_2$O as obtained from eq. (6) above, a figure Δ = 16,150 cm^{-1} for [Fe phen$_2$ox] and [Fe phen$_2$mal] may be estimated. This is close to $\Delta(^1A_1)$ in [Fe phen$_2$(NCS)$_2$], thus providing an explanation for the comparable infrared spectral properties of [Fe phen$_2$X$_2$] complexes in triplet ground states and in singlet ground states. However, it should be realized that a considerable mixing of most low lying levels is to be expected in the vicinity of the cross-over point. This mixing will be dependent on the octahedral as well as the low-symmetry ligand field, the spin–orbit coupling, and the electron repulsion parameters. The formation of a lowest electronic state which is, to a major part, a spin triplet, will thus occur by a suitable combination of all these parameters. More details are discussed elsewhere[28].

The situation where the crossing of electronic ground states occurs may be illustrated in terms of potential energy surfaces, since it is the molecules in their equilibrium geometries which are involved. Figure 1 shows schematically a section through the potential energy surfaces along the direction of the displacement coordinate for the totally symmetric metal–ligand stretching vibration (assuming the six metal–ligand distances in one ground state to be identical, r_0). It should be pointed out that, as demonstrated above, the two different molecular ground states will have, in general, different average distances r_0 and, therefore, different[52] splitting parameters $\Delta \sim r_0^{-5}$. The states $^5T_2$ and $^1A_1$ have an intersection area and their curves cross at the point P characterized by the mean crossing parameter Δ_P which may be approximated by π. Also, point P is assumed to have the energy E_{PA} above the absolute zero-point energy of the $^1A_1$ state and E_{PT} has the analogous meaning with respect to the $^5T_2$ state. At high temperatures, the complexes are in an excited vibrational level of $^5T_2$. With decreasing temperature, the total molecular energy follows the potential curve for the $^5T_2$ state eventually passing point P. At P, the configurations of $^5T_2$ and $^1A_1$ are identical, thus generating favorable conditions for a change-over between the two states. At this point, a true equilibrium between complexes in $^5T_2$ and $^1A_1$ ground states exists. If the temperature decreases further, it is of considerable importance whether the mole-

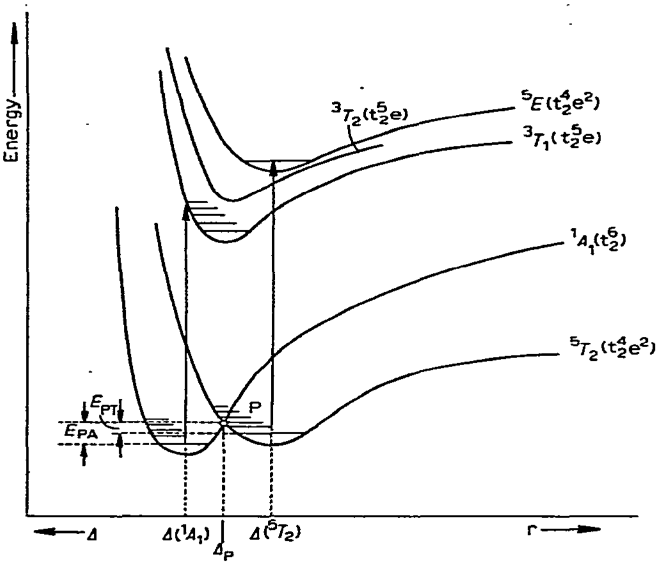


Fig. 1. Schematic potential energy curves for the lowest molecular states of a d^6 complex ion with almost equi-energetic ground states $^5T_2$ and $^1A_1$ (the lowest electronic transitions $^5E \leftarrow {}^5T_2$ and $^3T_1 \leftarrow {}^1A_1$ observed in the optical spectra are indicated).

cules are relatively free or are tightly bound in a lattice. In the first case, the distribution of molecules between the $^5T_2$ and $^1A_1$ states will depend essentially on the difference in zero-point energies, $\Delta E_0 = E_{PA} - E_{PT}$, and on the position of point P as determined by E_{PA} and E_{PT} separately. The second case, however, deserves particular attention.

We have shown above already how the nature of the crystal lattice influences the magnetic behaviour of the present compounds. Thus, in all three compounds studied, *viz.* [Fe dip$_2$(NCS)$_2$], [Fe phen$_2$(NCS)$_2$] and [Fe phen$_2$(NCSe)$_2$], the fraction of molecules which, even below T_c, remains in a $^5T_2$ ground state, is strongly dependent on the polymorph studied. In addition, some more subtle differences in the μ_{eff} *vs.* T curves are observed for the various polymorphs (*cf.* Fig. 1 in ref. 36). There are several recent reports of anomalous magnetic properties in iron(II) complexes which are suggestive of the $^5T_2 - {}^1A_1$ crossover. It is striking that, in all these instances, the magnetic behaviour of the iron(II) ion in the complex is determined by properties of the solid.

Thus the magnetic moments of [Fe papth$_2$]X$_2$, where papth = 2-(2-pyridylamino)-4-(2-pyridyl)thiazole, depend markedly on the associated[80] anion X. The iodide and perchlorate, *e.g.* (μ_{eff} = 5.00 and 5.14 BM, respectively, at ~304 °K), are clearly of high-spin type, whereas the chloride and bromide (μ_{eff} = 1.78 and 1.30 BM, respectively, at ~300 °K) are essentially of low-spin type. There are several examples of a pronounced temperature dependence of the moment (if X = SCN, *e.g.*, μ_{eff} = 4.82 BM at 339 °K and μ_{eff} = 2.25 BM at 136 °K) which have been rationalized in terms of $^5T_2 - {}^1A_1$ equilibria. It has also been demonstrated that the degree of hydration of these complexes can influence the magnetism of the cation. An anionic dependence of the moments has likewise been observed[78] for [Fe mephen$_3$]X$_2$ (mephen = 2-methyl-1,10-phenanthroline), where a $^5T_2$ ground state is formed, *e.g.*, if X = I, and where $^5T_2 - {}^1A_1$ equilibria are apparently present if X = ClO$_4$. Finally, even the solvent of crystallization may affect the magnetic behaviour to a great extent. The uncharged complex [Fe papth$_2$] (where papt denotes the anion resulting when a proton is lost from papth) was shown[81] to exhibit $^5T_2 - {}^1A_1$ equilibria (μ_{eff} = 4.96 BM at 310 °K and μ_{eff} = 1.55 BM at 94 °K), whereas the solvates [Fe papt$_2$] · C_6H_6 and [Fe papt$_2$] · $\frac{2}{3}$CHCl$_3$ are essentially of high-spin type.

The anion- and solvation-dependence of the magnetism may be derived presumably from differences in crystal packing. Since it is the same complex cation which is involved in all compounds compared, the variation in the energy difference between the ground states $^5T_2$ and $^1A_1$ has to be attributed to different lattice forces. Although such energy shifts may be quite common, their critical influence on the magnetism will become apparent only when nearly equi-energetic ground terms of different total spin exist. It may further be expected that d^6 ions will be particularly susceptible to crystal lattice effects, since the changeover between $t_2{}^6$ and $t_2{}^4e^2$ configurations is accompanied by a sizable increase in metal–

ligand bond length. It is of some interest, whether a given lattice can accomodate such changes. In [Fe dip$_2$(NCS)$_2$], the change in Fe-N(dip) bond length is ~0.14 Å[72] and no crystallographic phase change has been detected. In other compounds, various observations such as the rather sudden change[76] of μ_{eff} with T, the change in slope of ln *K vs.* $1/T$ plots[78,80], where *K* is the apparent equilibrium constant, or the time-dependence of μ_{eff} in the transition range[80] were cited as evidence of a phase change.

Even if a phase change is not involved, the apparent sensitivity of the energy separation between the ground terms to variations in the metal–ligand bond length would render the unreflected application of the Van Vleck equation unsuccessful. In the present case, the magnetic behaviour should be governed by a Boltzmann distribution over the Zeeman levels depicted in Fig. 2, if a true spin-state equilibrium and strict octahedral symmetry were realized. The susceptibility expression resulting therefrom has been derived previously[30]. If the conventional assumption of constant ΔE is used, the calculated curves of μ_{eff} *vs.* *T* vary between the limiting values of experimental magnetic moments (*cf.* Fig. 1 in ref. 30 and Fig. 1 in ref. 36). However, the sharp decrease of μ_{eff} at T_c is not reproduced correctly. Similar experience has been made on various systems of d^6 [78,80] and other configurations[52] displaying spin-state equilibria.

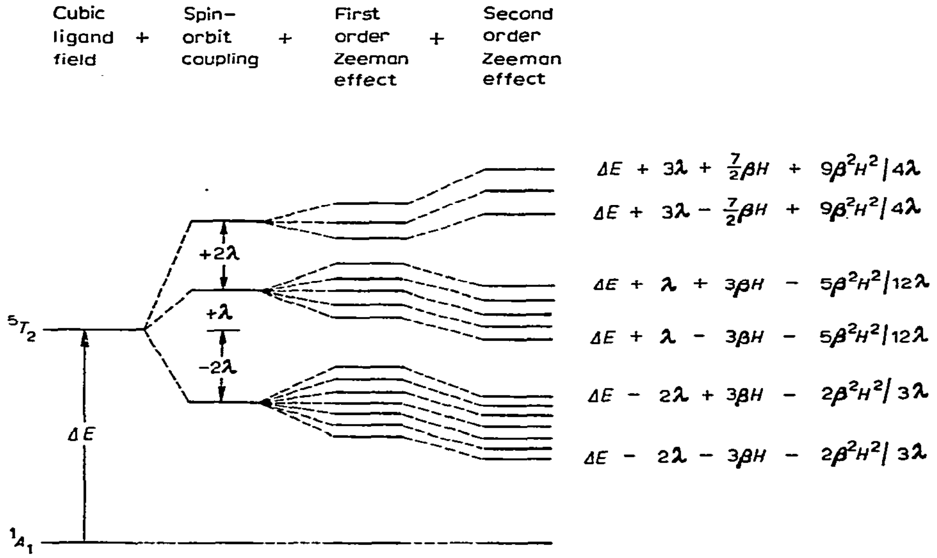


Fig. 2. Energy levels of a d^6 complex ion with close-lying ground states $^5T_2$ and $^1A_1$ in an octahedral field under the action of spin-orbit coupling, first and second order Zeeman effect. The energy expressions for the outermost final levels are indicated on the right hand side.

It has been pointed out only recently in a study of the crossover in poly(1-pyrazolyl)borate complexes of iron(II) by Jesson *et al.*[76] that the drop of the magnetic moment can only be explained if there is a very sharp temperature dependence of ΔE. It is plausible that, in the present case, a fully high-spin moment of $\sim$5.2 BM will be obtained, if the $^1A_1$ state is well above the $^5T_2$ state at room temperature, and that only the temperature-independent paramagnetism will contribute, if the $^1A_1$ state is well below the $^5T_2$ state at low temperatures. Indeed, the provision of a temperature variation of ΔE results in a reasonable fit to the experimental μ_{eff} *vs.* T curves[23]. Obviously, the positions of all energy levels and hence all energy separations are sensitive functions of the effective strength of the ligand field and thus of the metal–ligand distance. The assumed temperature dependence of ΔE then arises as a consequence of the change in bond length.

Palmer and Piper[66] observed that, in single crystals containing the $[\mathrm{Fe\ dip_3}]^{2+}$ ion, the intensity of the $(\mathrm{core})\pi^2 t_2{}^6 \rightarrow (\mathrm{core})\pi^2 t_2{}^5 \pi^{**}$ charge-transfer band increased on cooling from 300 to 80 °K. They suggested that this enhancement is caused by the decrease in the Fe–N bond length with decrease in temperature which would result in a greater degree of overlap and thus a greater d electron delocalization. Presumably such a change in the Fe–N distance could also occur in $[\mathrm{Fe\ dip_2(NCS)_2}]$ and similar complexes. It might be a reasonable working hypothesis to assume that this decrease in metal–ligand bond length initiates the change in electronic ground state. This then is followed by a further decrease in distance. If this model should prove to be correct, the complete temperature variation of ΔE would follow quite naturally.

ACKNOWLEDGMENTS

The author appreciates stimulating discussions with Dr. K. Madeja as well as with Dr. K. J. Watson who made a great effort to improve the manuscript.

REFERENCES

1 F. Blau, *Ber.*, 21 (1888) 1077.
2 F. Blau, *Monatsch. Chem.*, 19 (1898) 647.
3 W. Brandt, F. P. Dwyer and E. C. Gyarfas, *Chem. Revs.*, 54 (1954) 959.
4 L. F. Lindoy and S. E. Livingstone, *Coordin. Chem. Rev.*, 2 (1967) 173.
5 C. K. Jørgensen, *Inorganic Complexes*, Academic Press, London and New York, 1963.
6 F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, (1952) 3570.
7 F. Hein and S. Herzog, *Z. Anorg. Allgem. Chem.*, 267 (1952) 337.
8 H. Irving and D. H. Mellor, *J. Chem. Soc.*, (1962) 5222 and 5237.
9 K. Madeja and E. König, *J. Inorg. Nucl. Chem.*, 25 (1963) 377.
10 A. A. Schilt, *J. Am. Chem. Soc.*, 82 (1960) 3000.
11 W. Beck and E. Schuierer, *Ber.*, 95 (1962) 3048.
12 A. A. Schilt and K. Fritsch, *J. Inorg. Nucl. Chem.*, 28 (1966) 2677.
13 W. Klemm, H. Jacobi and W. Tilk, *Z. Anorg. Allgem. Chem.*, 201 (1931) 1.
14 F. Basolo and F. P. Dwyer, *J. Am. Chem. Soc.*, 76 (1954) 1454.
15 K. Madeja, *Habilitationsschrift*, University of Greifswald, Germany, 1964.

16 K. Madeja, W. Wilke and S. Schmidt, *Z. Anorg. Allgem. Chem.*, 346 (1966) 306.
17 W. A. Baker, Jr. and H. M. Bobonich, *Inorg. Chem.*, 2 (1963) 1071.
18 K. Madeja and W. Wilke, to be published.
19 P. Job, *Ann. Chim. Phys.*, 9 (1928) 113.
20 A. A. Schilt, *J. Am. Chem. Soc.*, 82 (1960) 5779.
21 N. K. Hamer and L. E. Orgel, *Nature*, 190 (1961) 439.
22 D. F. Shriver, *J. Am. Chem. Soc.*, 85 (1963) 1405.
22a D. F. Shriver and J. Posner, *J. Am. Chem. Soc.*, 88 (1966) 1672.
22b J. J. Rupp and D. F. Shriver, *Abstract of Paper 151st ACS Meeting* (1966).
22c D. F. Shriver, *Structure and Bonding*, 1 (1966) 32.
23 E. König, unpublished results.
24 J. S. Griffith, *J. Inorg. Nucl. Chem.*, 2 (1956) 1.
25 Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, 9 (1954) 753, 766.
26 E. König, A. S. Chakravarty and K. Madeja, *Theoret. Chim. Acta*, 9 (1967) 171.
27 W. A. Baker, Jr. and H. M. Bobonich, *Inorg. Chem.*, 3 (1964) 1184.
28 E. König and K. Madeja, *Inorg. Chem.*, 7 (1968) 1848.
29 E. König and K. Madeja, *J. Am. Chem. Soc.*, 88 (1966) 4528.
30 E. König and K. Madeja, *Inorg. Chem.*, 6 (1967) 48.
31 E. König and K. Madeja, *Chem. Commun.*, (1966) 61.
32 L. Cambi and A. Cagnasso, *Atti Accad. Nazl. Lincei*, 19 (1934) 458.
33 S. Sugden, *J. Chem. Soc.*, (1943) 328.
34 H. Irving and D. H. Mellor, *J. Chem. Soc.*, (1962) 5222.
35 K. Madeja, *Chem. Zvesti*, 19 (1965) 186.
36 E. König, K. Madeja and K. J. Watson, *J. Am. Chem. Soc.*, 90 (1968) 1146.
37 F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, (1952) 3570.
38 E. König and A. S. Chakravarty, *Theoret. Chim. Acta*, 9 (1967) 161.
39 L. R. Walker, G. K. Wertheim and V. Jaccarino, *Phys. Rev. Letters*, 6 (1961) 98.
40 V. I. Goldanskii, *The Mössbauer Effect and its Applications in Chemistry*, Consultants Bureau, New York, 1964.
41 O. C. Kistner and A. W. Sunyar, *Phys. Rev. Letters*, 4 (1960) 412.
42 E. König, S. Hüfner, E. Steichele and K. Madeja, *Z. Naturforsch.*, 22a (1967) 1543; *ibid.* 23a (1968) 632.
43 J. F. Duncan and K. F. Mok, *J. Chem. Soc.*, (1966) 1493.
44 R. M. Golding, K. F. Mok and J. F. Duncan, *Inorg. Chem.*, 5 (1966) 774.
45 L. M. Epstein, *J. Chem. Phys.*, 40 (1964) 435.
46 P. R. Brady, J. F. Duncan and K. F. Mok, *Proc. Roy. Soc.*, A 287 (1965) 343.
47 R. L. Collins, R. Pettit and W. A. Baker, Jr., *J. Inorg. Nucl. Chem.*, 28 (1966) 1001.
48 W. A. Baker, private communication.
49 E. König and S. Hüfner, unpublished results.
50 I. Dezsi, B. Molnar, T. Tarnoczi and K. Tompa, *J. Inorg. Nucl. Chem.*, 29 (1967) 2486.
51 E. Frank and C. R. Abeledo, *Inorg. Chem.*, 5 (1966) 1453.
52 A. H. Ewald, R. L. Martin, I. G. Ross and A. H. White, *Proc. Roy. Soc.*, A 280 (1964) 235.
53 J. P. Jesson and J. F. Weiher, *J. Chem. Phys.*, 46 (1967) 1995.
54 L. M. Epstein, *J. Chem. Phys.*, 36 (1962) 2731.
55 A. B. P. Lever, *J. Chem. Soc.*, (1965) 1821.
56 A. Hudson and H. J. Whitfield, *Chem. Commun.*, (1966) 606.
57 E. König and K. Madeja, unpublished results.
58 A. A. Schilt, *Inorg. Chem.*, 3 (1964) 1323.
59 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, J. Wiley, New York and London, 1963.
60 D. A. Buckingham, F. P. Dwyer, H. A. Goodwin and A. M. Sargeson, *Austral. J. Chem.*, 17 (1964) 325.
61 R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, 4 (1965) 350.
62 C. W. Frank and L. B. Rogers, *Inorg. Chem.*, 5 (1966) 615.
63 E. König and K. Madeja, *Spectrochim. Acta*, 23A (1967) 45.
64 J. R. Ferraro, L. J. Basile and D. L. Kovacic, *Inorg. Chem.*, 5 (1966) 391.

65 P. Spacu and C. Lepadatu, *J. Am. Chem. Soc.*, 88 (1966) 3221.
66 R. A. Palmer and T. S. Piper, *Inorg. Chem.*, 5 (1966) 864.
67 E. König and H. L. Schläfer, *Z. Physik. Chem. (Frankfurt)*, 34 (1962) 355.
68 R. J. P. Williams, *J. Chem. Soc.*, (1955) 137.
69 P. Day and N. Sanders, *J. Chem. Soc.*, (1967) 1530.
70 P. Day and N. Sanders, *J. Chem. Soc.*, (1967) 1536.
71 H. L. Schläfer, *Z. Physik. Chem. (Frankfurt)*, 8 (1956) 373.
71a H. L. Schläfer and E. König, *Z. Physik. Chem. (Frankfurt)*, 19 (1959) 265.
72 K. J. Watson and E. König, to be published.
73 M. A. Robinson, J. D. Curry and D. H. Busch, *Inorg. Chem.*, 2 (1963) 1178.
74 C. K. Jørgensen, *Absorption Spectra and Chemical Bonding in Complexes*, Pergamon Press, London, 1962.
75 C. K. Jørgensen, *Adv. Chem. Phys.*, 5 (1963) 33.
76 J. P. Jesson, J. F. Weiher and S. Trofimenko, *J. Chem. Phys.*, 48 (1968) 2058.
77 A. T. Casey and F. Isaacs, *Austral. J. Chem.*, 20 (1967) 2765.
78 H. A. Goodwin and R. N. Sylva, *Austral. J. Chem.*, 21 (1968) 83.
79 J. H. van Santen and J. S. van Wieringen, *Rec. Trav. Chim.*, 71 (1952) 420.
80 R. N. Sylva and H. A. Goodwin, *Austral. J. Chem.*, 20 (1967) 479.
81 R. N. Sylva and H. A. Goodwin, *Austral. J. Chem.*, 21 (1968) 1081.