Studies of Spin Crossover in some Tris[2-(2′-pyridyl)benzimidazole]iron(II) Complexes

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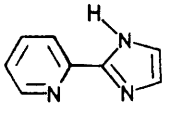
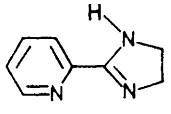
Four complexes of the bidentate chelating ligand 2-(2′-pyridyl)benzimidazole (pbim) are described: $[Fe(pbim)_3]Br_2$; $[Fe(pbim)_3][NO_3]_2{\cdot}OH_2$; and $[Fe(pbim)_3][ClO_4]_2{\cdot}xOH_2$ ($x = 1$ or 2). The complexes have been characterized by Mössbauer spectra (4.2—300 K), susceptibility measurements (80—310 K), solid-state (80—300 K) and solution visible spectra (298 K), and conductance measurements and i.r. spectra (295 K). All four complexes exhibit $^5T_{2g}$–$^1A_{1g}$ spin crossover, the details of which are sensitive to the nature of the anion and, for the perchlorate derivatives, the number of molecules of water of crystallization. The latter effect is attributed to hydrogen bonding between water molecules and the imino-hydrogen atom of the ligand. From magnetic-perturbation Mössbauer spectra, it is deduced that the $[Fe(pbim)_3]^{2+}$ cation has a *mer*-octahedral configuration in both spin states, indicating substantial inequivalence of the pyridine and imidazole nitrogen atoms in the pbim ligand.

SINCE the first observations of $^5T_{2g}$–$^1A_{1g}$ spin crossover in octahedral d^6 iron(II) complexes were reported for $[Fe(phen)_2(NCX)_2]$ (phen = 1,10-phenanthroline, X = S or Se) [1,2] a number of other iron(II) complexes have been shown to exhibit such a spin equilibrium.[3-12] In every case Fe^{II} is co-ordinated to six nitrogen atoms. Although details vary significantly from one system to another, there are at least two features which are common to all cases of $^5T_{2g}$–$^1A_{1g}$ transitions observed to date. First, it is not possible to interpret the crossover simply in terms of changes in thermal population of close-lying $^5T_{2g}$ and $^1A_{1g}$ manifolds. Secondly, ^{57}Fe Mössbauer spectra always show lines due to both $S = 0$ and 2 spin states in the transition region, indicating that the electronic relaxation rate is slow compared to the Larmor precession frequency of the iron-57 nucleus.


pim


H_2pim

Certain iron(II) complexes of both 2-(2′-pyridyl)-imidazole (pim) and 2-(2′-pyridyl)-2-imidazoline (H_2pim) show $^5T_{2g}$–$^1A_{1g}$ crossover,[10-12] but there are important differences in the behaviour of the two systems. For example, $[Fe(H_2pim)_3][ClO_4]_2$ exists as two magnetic isomers;[10] one is diamagnetic at and below 295 K, whereas the other shows an abrupt change in magnetic moment at *ca.* 120 K. The Mössbauer spectrum of the last isomer at 80 K shows lines due to both high- and low-spin Fe^{II}, with only the high-spin species present at 294 K. On the other hand, $[Fe(pim)_3][ClO_4]_2{\cdot}OH_2$ [11] and several other $[Fe(pim)_3]^{2+}$ salts [12] show very gradual changes in magnetic moment with temperature. The $\mu_{eff.}$ values do not exceed *ca.* 4.0 B.M. at room temperature and are in the range 0.6—2.9 B.M. at *ca.* 90 K.† Mössbauer spectra of all the pim complexes studied thus far indicate a greater population of the $S = 0$ state at 295 K.

The ligands pim and H_2pim are of particular interest because the NH group on the imidazole ring shows changes in acidity when the ligands are chelated to various metals.[13] Moreover, the marked differences in behaviour of the $[Fe(pim)_3]^{2+}$ and $[Fe(H_2pim)_3]^{2+}$ complexes show that the crossover phenomenon is very sensitive to minor changes in the ligand structure. It seemed of interest to study some iron(II) complexes of the closely related compound 2-(2′-pyridyl)benzimidazole (pbim). If these complexes were found to show high-spin–low-spin crossover, they might provide more information on

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† 1 B.M. ≈ 9.27×10^{-24} A m², 1 bar = 10^5 Pa, 1 G = 10^{-4}T.

[1] E. König and K. Madeja, *Chem. Comm.*, 1966, 61.

[2] E. König and K. Madeja, *Inorg. Chem.*, 1967, **6**, 48.

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[4] E. König, K. Madeja, and K. J. Watson, *J. Amer. Chem. Soc.*, 1968, **90**, 1146.

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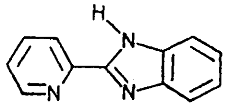
[11] D. M. L. Goodgame and A. A. S. C. Machado, *Inorg. Chem.*, 1969, **8**, 2031.

[12] R. J. Dosser, W. J. Eilbeck, A. E. Underhill, P. R. Edwards, and C. E. Johnson, *J. Chem. Soc.* (*A*), 1969, 810.

[13] T. R. Harkins and H. Freiser, *J. Amer. Chem. Soc.*, 1956, **78**, 1143.

the possible influence of the imino-hydrogen atom on the transition characteristics. Furthermore, the asymmetric nature of the ligand might lead to larger distortions of the iron environment, which in turn might tell us



pbim

more about the cation structure. This paper reports studies of four such complexes: $[Fe(pbim)_3]Br_2$, $[Fe(pbim)_3][NO_3]_2\cdot OH_2$, and $[Fe(pbim)_3][ClO_4]_2\cdot xOH_2$ (x = 1 or 2).[14] All four are found to show spin equilibria, and the details are strongly affected by the nature of the anion, and, in the case of the perchlorate complexes, the number of water molecules of crystallization.

RESULTS AND DISCUSSION

With the exception of $[Fe(pbim)_3][ClO_4]_2\cdot OH_2$, which converts into the dihydrate on exposure to atmospheric moisture, the complexes are air stable. The lack of any tendency to oxidize to iron(III) species is presumably due to the bulkiness of the ligands, which make Fe^{II} inaccessible to oxidative attack. The perchlorate dihydrate reverts readily to the monohydrate at room temperature on the vacuum line. However, attempts to remove the water of crystallization from either of the monohydrates by heating weighed samples to 150 °C *in vacuo* for 6 h were unsuccessful: no appreciable weight loss was observed in either case. The presence of water after heating the samples *in vacuo* was also confirmed by the appearance of bands at *ca.* 3 300 cm^{-1} in the i.r. spectra.

The molar conductances of the complexes in methanol lie within the range expected for 10^{-3} mol dm^{-3} solutions of 2 : 1 electrolytes in this solvent (160—222 S cm^2 mol^{-1}).[15] The values observed (160—188 S cm^2 mol^{-1}) are at the lower end of this range, which can be attributed to the large mass of the cation. In the solid state all four complexes undergo a dramatic colour change (orange or brown to purple) when cooled to liquid-nitrogen temperature. However, no colour change was observed on freezing methanol solutions of the complexes. This will be discussed in more detail below.

Infrared Spectra.—The i.r. spectra of pbim and some of its metal complexes have been studied by Lane *et al.*,[16] and the spectra of our iron complexes are similar to those of other transition-metal complexes with this ligand. Pyridine ring bands[17] at 996, 1 046, 1 154, and 1 279 cm^{-1} are all shifted upwards by *ca.* 10 cm^{-1} in the complexes, showing the involvement of the pyridine nitrogen in bonding to iron. In the free ligand there is a strong band at 1 314 cm^{-1} which splits into a doublet on chelation.[16] In the iron complexes this doublet appeared at 1 324 and 1 302 cm^{-1}. We regard this as an indication that the imidazole nitrogen atom is also involved in bonding to iron. Bands which can be assigned to the $[Fe(pbim)_3]^{2+}$ cation were identical for all four complexes.

For $[Fe(pbim)_3][NO_3]_2\cdot OH_2$, the ν_3 band of the nitrate ion was split by 59 cm^{-1}. This splitting is small compared to those found for co-ordinated nitrate groups (typically *ca.* 200 cm^{-1}),[18] and can probably be attributed to a lattice distortion. The ν_1 and ν_2 anion modes appeared as very weak bands at 1 038 and 825 cm^{-1}, respectively, while ν_4 is probably masked by a broad ligand absorption at 744 cm^{-1}.

The complexes $[Fe(pbim)_3][ClO_4]_2\cdot xOH_2$ (x = 1 or 2) gave identical i.r. spectra in the range 250—3 200 cm^{-1}, and both showed a band due to water of crystallization at 3 180 cm^{-1}. The dihydrate had an additional band at 3 500 cm^{-1} which could be eliminated by evacuating the sample at room temperature. In both complexes the ν_3 perchlorate band[18] centred at *ca.* 1 038 cm^{-1} was split by 60 cm^{-1}. (This can be compared to $HClO_4$ where the ν_3 splitting is 280 cm^{-1}.)[19] The moderate splitting seen here is probably due to a small distortion of the $[ClO_4]^-$ anion by lattice effects. The ν_4 band of $[ClO_4]^-$ is not split at 624 cm^{-1}, while ν_1 and ν_2 are assigned to very weak bands at 968 and 458 cm^{-1}, respectively.

Magnetic Data.—Molar susceptibilities (χ_M) and effective magnetic moments ($\mu_{eff.}$) of the complexes between 80 and 300 K are listed in Table 1. All four complexes showed moments of *ca.* 5.4 B.M. at room temperature as expected for high-spin Fe^{2+}, but the temperature dependence of $\mu_{eff.}$ is anomalous and varied markedly from complex to complex. However, there is no obvious correlation between $\mu_{eff.}$ and the nature of the anion. Curie–Weiss behaviour was not observed for any of the four complexes.

The magnetic data by themselves do not establish the existence of high-spin–low-spin equilibria, although antiferromagnetic iron–iron interactions (which could also cause such anomalous magnetic behaviour) seem very unlikely in these systems. However, Mössbauer data presented below definitely show the presence of Fe^{II} in both $^5T_{2g}$ and $^1A_{1g}$ states, and that the relative populations of the two states depend on the temperature, the nature of the anion, and the degree of hydration. Thus, we will discuss the magnetic-moment data in terms of the effects of these three variables on the composition of the high-spin–low-spin ' mixture '.

The temperature dependence of $\mu_{eff.}$ for $[Fe(pbim)_3][NO_3]_2\cdot OH_2$ is not unusually large for a pure high-spin iron(II) complex, although the Mössbauer spectra show there are some molecules in the $^1A_{1g}$ ground state below *ca.* 180 K. For the bromide salt the moment at 80 K

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[14] A preliminary communication on three of these complexes has appeared: J. R. Sams, J. C. Scott, and T. B. Tsin, *Chem. Phys. Letters*, 1973, **18**, 451.

[15] W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81.

[16] T. J. Lane, I. Nakagawa, J. L. Walter, and A. J. Kandathil, *Inorg. Chem.*, 1962, **1**, 267.

[17] J. H. S. Green, W. Kynaston, and H. M. Paisley, *Spectrochim. Acta*, 1963, **19**, 549.

[18] K. Nakamoto, ' Infrared Spectra of Inorganic and Coordination Compounds,' Wiley, New York, 1963.

[19] B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 1961, 3091.

was *ca.* 3.6 B.M., indicating that there is still a substantial fraction of the high-spin species at this temperature. Perhaps the most interesting results are those for the perchlorate complexes, where both the mono- and dihydrate were obtained. The complex $[Fe(pbim)_3][ClO_4]_2{\cdot}OH_2$ had a moment of 5.44 B.M. at 300 K, which decreased to 2.00 B.M. at 80 K. On introduction of a second water molecule into the lattice, the room-temperature moment decreased slightly to 5.35 B.M., while at 80 K $\mu_{eff.}$ was only 1.29 B.M. It thus appears that the second water molecule increases the fraction of low-spin species at all temperatures. When the dihydrate was reconverted into the monohydrate on the vacuum line, the original $\mu_{eff.}$ against T curve for the monohydrate was exactly restored. Dosser *et al.*[12] also observed that the magnetic moments of $[Fe(pim)_3][SO_4]{\cdot}xOH_2$ ($x = 2$ or 3) were somewhat different (the trihydrate giving lower $\mu_{eff.}$ values), but gave no discussion of this behaviour.

TABLE 1

Molar susceptibilities and effective magnetic moments of the complexes

Complex	T/K	$10^3\chi_M$/ c.g.s. units	$\mu_{eff.}$/B.M.
$[Fe(pbim)_3][ClO_4]_2{\cdot}OH_2$	79.8	6.268	2.00
	90.7	5.795	2.05
	106.2	5.549	2.17
	124.0	5.812	2.40
	139.7	6.373	2.67
	157.0	7.441	3.06
	181.4	10.856	3.97
	202.9	15.673	5.04
	221.0	15.865	5.30
	245.4	14.867	5.40
	264.5	13.956	5.43
	284.4	13.028	5.44
	306.4	12.030	5.43
$[Fe(pbim)_3][ClO_4]_2{\cdot}2OH_2$	80.5	2.581	1.29
	95.0	2.334	1.33
	113.4	2.391	1.47
	134.0	2.562	1.66
	153.4	3.018	1.92
	170.0	3.535	2.19
	190.5	4.443	2.60
	208.3	5.626	3.06
	229.5	7.377	3.68
	251.4	9.855	4.45
	267.9	11.204	4.90
	290.3	11.760	5.23
	310.5	11.527	5.35
$[Fe(pbim)_3][NO_3]_2{\cdot}OH_2$	79.0	37.373	4.86
	98.6	31.276	4.97
	125.1	25.658	5.07
	152.5	21.904	5.17
	179.7	19.278	5.26
	204.7	17.087	5.29
	231.4	15.315	5.32
	264.5	13.517	5.35
	278.8	12.828	5.35
	296.0	12.089	5.35
$[Fe(pbim)_3]Br$	80.4	20.657	3.65
	94.0	19.689	3.85
	104.5	19.336	4.02
	116.4	18.955	4.20
	128.3	18.720	4.38
	138.8	18.573	4.54
	149.3	18.529	4.70
	163.1	18.339	4.89
	174.6	18.016	5.02
	185.0	17.664	5.11
	194.4	17.282	5.18
	219.7	15.932	5.29
	241.1	14.905	5.36
	263.0	13.936	5.41
	287.1	12.880	5.44

During the course of this work, Sasaki and Shigematsu[20] reported magnetic-susceptibility data for $[Fe(pbim)_3][ClO_4]_2{\cdot}OH_2$. Although these workers suggest the occurrence of a $^5T_{2g}$–$^1A_{1g}$ spin equilibrium in the complex, their magnetic-moment data are very different from ours. In particular, they report $\mu_{eff.}$ values of 5.25 and 3.33 B.M. at 298 and 77.2 K respectively, compared to our values of 5.43 (306.4) and 2.00 B.M. (79.8 K). We suggest that the discrepancy is probably due to the existence of more than one magnetic isomer of $[Fe(pbim)_3][ClO_4]_2{\cdot}OH_2$ {similar to the situation in $[Fe(H_2pim)_3][ClO_4]_2$ mentioned above},[10] and that we and Sasaki and Shigematsu[20] have obtained and studied different isomers. Their preparative procedure involved mixing ethanol solutions of pbim and $FeCl_2{\cdot}4OH_2$, followed by addition of perchloric acid and then water. Three separate preparations of this complex by our route described below gave consistent and reproducible magnetic and Mössbauer data, but we observed that addition of small amounts of acid to a reaction mixture can change the low-temperature moments of these salts by 20% or more.

Electronic Spectra.—In methanol solution at 25 °C the electronic spectra of all four complexes were nearly identical. There was a strong ligand band at 330 nm ($\varepsilon_{max.} \approx 1.2 \times 10^4$ dm^3 mol^{-1} cm^{-1}) and a weaker absorption at 490 nm ($\varepsilon_{max.} \approx 1 \times 10^3$ dm^3 mol^{-1} cm^{-1}). The assignment of the 490 nm band to the *d–d* transition $^5T_{2g} \rightarrow {}^5E_g$ gives a $10Dq$ value of *ca.* 20 000 cm^{-1}, as expected for intermediate ligand fields near the high-spin–low-spin crossover point. However, the intensity of the band is abnormally high for a *d–d* transition. This may be a result of ' intensity stealing '[21] from the 330 nm ligand band. An alternative explanation is that the 490 nm band arises from a $t_{2g} \rightarrow \pi^*$ charge-transfer transition, but if this is the case the intensity is an order of magnitude smaller than normally observed for such transitions.[21]

An interesting feature of the solution electronic spectra is that the 490 nm bands have very similar absorption coefficients for all four complexes despite the differences in their magnetic behaviour in the solid state. We mentioned above that the solid complexes change colour on cooling, whilst their methanol solutions do not. These observations strongly suggest that the $^5T_{2g}$–$^1A_{1g}$ crossover is exclusively a solid-state effect, and it was of interest, therefore, to study the temperature dependence of the electronic spectra of these complexes in the form of solid KBr pellets. Solid-state spectral data are given in Table 2.

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[20] Y. Sasaki and T. Shigematsu, *Bull. Chem. Soc. Japan*, 1973, **46**, 3438.

[21] B. N. Figgis, ' Introduction to Ligand Fields,' Interscience, New York, 1966.

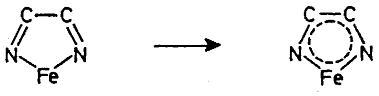
At room temperature, in addition to the strong ligand band at 330 nm, each spectrum contained a weak feature at *ca.* 490 nm, which shifted to slightly longer wavelength and increased in intensity as the temperature was lowered. For the nitrate derivative the intensity of the latter band showed a sudden jump below *ca.* 200 K, coincident with the appearance of another band of equal intensity at *ca.* 540 nm. The intensities of both bands remained essentially constant on further cooling. For the bromide complex there was a sharp increase in intensity of the 490 nm band at *ca.* 250 K, but there was no clear separation into two bands until the temperature was lowered to *ca.* 180 K. For the perchlorate monohydrate, only the 540 nm band was seen clearly below *ca.* 240 K, and its intensity continued to rise with decreasing temperature.

TABLE 2

Solid-state visible bands of the complexes as a function of temperature

		$\lambda_{max.}$/nm		Intensity (arbitrary units)	
Complex	T/K	Band 1	Band 2	Band 1	Band 2
$[Fe(pbim)_3][ClO_4]_2{\cdot}OH_2$	88		544		22.4
	107		544		21.0
	128		544		18.8
	172		538		14.0
	185		538		12.4
	208		534		10.1
	223		530		8.2
	235		530		6.4
	246	510		3.2	
	257	510		3.2	
	263	510		3.0	
	273	510		2.4	
	293	505		1.3	
	303	495		0.8	
	313	490		0.2	
	323	490		0.2	
$[Fe(pbim)_3][NO_3]_2{\cdot}OH_2$	79	500	545	4.8	4.8
	103	500	545	4.8	4.8
	134	500	545	4.8	4.9
	167	505	540	4.8	4.8
	171	505	540	4.9	4.9
	194	500	540	4.8	4.8
	213	500	535	4.2	4.2
	224	500		1.8	
	241	500		1.8	
	254	490		1.5	
	268	495		1.4	
	298	490		1.3	
	320	485		0.9	
	327	485		0.8	
$[Fe(pbim)_3]Br_2$	103	505	544	9.2	9.6
	147	505	543	9.0	9.8
	157	505	540	9.1	9.5
	168	505	538	9.0	9.2
	179	505	535	9.0	9.0
	185	515		8.8	
	193	515		8.6	
	204	515		8.4	
	217	510		8.0	
	227	505		7.2	
	234	505		7.0	
	247	500		6.8	
	255	498		1.8	
	261	490		1.6	
	273	490		1.7	
	293	490		1.3	

The 540 nm absorption at low temperature is obviously responsible for the colour changes observed in these complexes. Moreover, the temperature at which this band appears is approximately the same as that at which the presence of a low-spin species can be detected in the Mössbauer spectra, and the intensities show a qualitative correlation with the fraction of $^1A_{1g}$ molecules deduced from Mössbauer area ratios (*see below*). This 540 nm band is almost certainly due to a charge-transfer transition involving the ligand π^* orbitals. The intensity and position of the band are characteristic of a unique class of compounds containing ' methine chromophores '.[22] The appearance of this band has been attributed to the formation of a five-membered aromatic ring system in which the iron t_{2g} electrons contribute substantially to the π-electron resonance system of the methine chromophore. This chromophore is known to arise only for a low-spin ground state in iron(II) complexes,[22] which confirms that the 540 nm band is associated with the $^1A_{1g}$ species.



Mössbauer Data.—The ^{57}Fe Mössbauer parameters for the complexes are listed in Table 3. Most spectra obtained for this series of complexes consisted of four lines, which could readily be identified as two quadrupole doublets, and the relative intensities of these doublets changed with temperature. This behaviour is illustrated in Figure 1 where spectra obtained for $[Fe(pbim)_3]$-$[ClO_4]_2{\cdot}OH_2$ between 4.2 and 295 K are shown. At 250

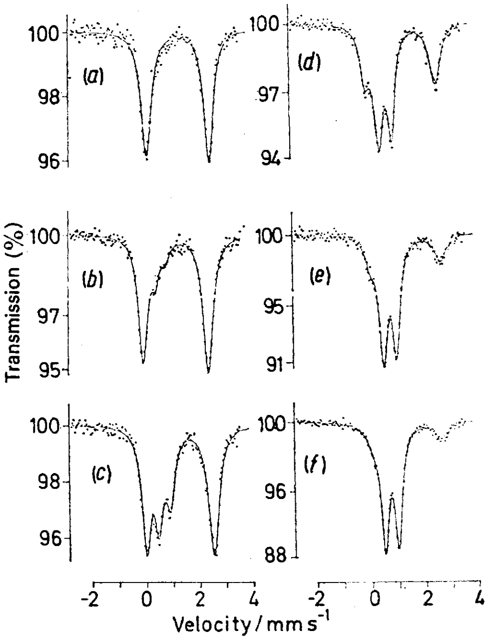


FIGURE 1 Mössbauer spectra of $[Fe(pbim)_3][ClO_4]_2{\cdot}OH_2$ at 250 (*a*), 220 (*b*), 200 (*c*), 180 (*d*), 130 (*e*), and 8.7 K. In the four-line spectra the inner pair of lines corresponds to the $S = 0(^1A_{1g})$ ground state and the outer pair to the $S = 2$ $(^5T_{2g})$ ground state

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[22] D. H. Busch and J. C. Bailar, *J. Amer. Chem. Soc.*, 1956, **78**, 1137.

K and above only one pair of lines is seen, with δ and $|\Delta E_Q|$ values in the ranges commonly observed for high-spin iron(II) salts. At 230 K two weak shoulders appear on the low-velocity line of the high-spin doublet. With further lowering of the temperature, the inner pair of lines gains intensity relative to the outer pair. The parameters (δ and $|\Delta E_Q|$) of the inner doublet are typical of those expected for low-spin iron(II) derivatives. Thus, the Mössbauer spectra show unequivocally the existence of temperature-dependent $^5T_{2g}$–$^1A_{1g}$ spin equilibria in these complexes. It can also be seen from Figure 1 that the transition in $[Fe(pbim)_3][ClO_4]_2{\cdot}OH_2$ is spread over at least 100 °C and, moreover, that there is an incomplete change in spin state since the high-spin component is still present at 4.2 K. For all the complexes, δ and $|\Delta E_Q|$ values for the high-spin species are very similar both in magnitude and temperature dependence, and the nature of the anion appears to have little or no effect on these parameters. The same is true of the parameters for the low-spin species. However, the relative intensities of the two doublets are strongly dependent on the nature of the anion and, for the perchlorate complexes, on the number of water molecules of crystallization.

In order to estimate the relative amounts of high- and low-spin species present at a given temperature, one can define an 'area fraction' (a.f.) as the area under the $^5T_{2g}$ pair of lines divided by the total spectral area. A.f. values are listed in the final column of Table 3.

TABLE 3

^{57}Fe Mössbauer parameters (mm s^{-1}) for the complexes

Complex		$S = 0$				$S = 2$				
	T/K	δ *	ΔE_Q	Γ_1	Γ_2	δ *	ΔE_Q	Γ_1	Γ_2	Area fraction
$[Fe(pbim)_3][ClO_4]_2{\cdot}OH_2$	4.2	0.75	0.48	0.23	0.23	1.37	2.46	0.39	0.39	0.23
	84	0.75	0.48	0.25	0.25	1.36	2.52	0.33	0.33	0.16
	100	0.75	0.48	0.25	0.25	1.36	2.56	0.33	0.37	0.20
	130	0.75	0.47	0.27	0.27	1.34	2.56	0.32	0.35	0.22
	160	0.74	0.46	0.27	0.30	1.33	2.51	0.40	0.38	0.31
	180	0.73	0.46	0.29	0.25	1.31	2.53	0.31	0.36	0.38
	190	0.73	0.45	0.29	0.27	1.30	2.51	0.32	0.35	0.45
	200	0.73	0.44	0.29	0.28	1.30	2.49	0.33	0.36	0.63
	210	0.70	0.41	0.24	0.24	1.30	2.47	0.32	0.36	0.77
	220	0.72	0.38	0.24	0.24	1.30	2.44	0.33	0.35	0.87
	230	0.66	0.38	0.24	0.24	1.29	2.42	0.32	0.35	0.90
	250					1.29	2.30	0.36	0.33	1.00
	295					1.25	2.17	0.34	0.33	1.00
$[Fe(pbim)_3][ClO_4]_2{\cdot}2OH_2$	4.2	0.75	0.46	0.25	0.25					0
	85	0.74	0.46	0.25	0.25					0
	120	0.75	0.47	0.23	0.23	1.36	2.56	0.36	0.36	0.18
	160	0.74	0.45	0.25	0.24	1.34	2.54	0.36	0.36	0.27
	180	0.73	0.46	0.25	0.27	1.33	2.56	0.38	0.38	0.34
	200	0.73	0.44	0.25	0.25	1.31	2.52	0.38	0.38	0.48
	220	0.76	0.48	0.29	0.28	1.25	2.51	0.33	0.33	0.57
	240	0.78	0.43	0.29	0.29	1.28	2.42	0.34	0.33	0.69
	293	0.75	0.42	0.25	0.26	1.25	2.21	0.36	0.33	0.84
$[Fe(pbim)_3][NO_3]_2{\cdot}OH_2$	4.2	0.78	0.45	0.28	0.28	1.36	2.52	0.36	0.40	0.80
	40	0.78	0.44	0.27	0.25	1.36	2.62	0.34	0.36	0.81
	85	0.74	0.42	0.29	0.29	1.35	2.65	0.34	0.36	0.82
	100	0.74	0.37	0.29	0.29	1.36	2.63	0.34	0.35	0.86
	120	0.72	0.32	0.29	0.29	1.36	2.60	0.34	0.35	0.90
	150	0.67	0.29	0.26	0.26	1.34	2.56	0.32	0.34	0.92
	180					1.34	2.45	0.34	0.34	1.00
	210					1.32	2.35	0.31	0.32	1.00
	240					1.31	2.27	0.33	0.34	1.00
	270					1.30	2.17	0.33	0.30	1.00
	295					1.24	1.89	0.33	0.29	1.00
$[Fe(pbim)_3]Br_2$	4.2	0.77	0.45	0.27	0.25	1.38	2.56	0.28	0.31	0.41
	40	0.76	0.44	0.26	0.24	1.38	2.64	0.27	0.28	0.41
	84	0.76	0.44	0.25	0.24	1.38	2.68	0.28	0.28	0.41
	110	0.74	0.43	0.25	0.24	1.36	2.66	0.28	0.28	0.50
	140	0.73	0.41	0.24	0.24	1.35	2.63	0.26	0.29	0.61
	170	0.73	0.37	0.25	0.25	1.33	2.57	0.30	0.29	0.72
	200	0.72	0.38	0.25	0.25	1.32	2.49	0.30	0.29	0.83
	230	0.68	0.34	0.24	0.25	1.30	2.46	0.30	0.29	0.87
	260					1.30	2.37	0.35	0.31	1.00
	293					1.25	2.23	0.32	0.28	1.00

* Isomer shift relative to disodium pentacyanonitrosylferrate(II) dihydrate.

It is important to realize that in equating the a.f. to the actual fraction of high-spin ions present one is tacitly assuming that the recoil-free fractions are identical for both high- and low-spin species in a given sample. This assumption may not be strictly valid, but it seems improbable that the recoil-free fractions for the two spin states will differ appreciably. In practice, when the a.f. is very close to zero or unity, statistical error introduced from fitting of the Mössbauer spectrum makes its estimation difficult. However, within the range $0.1 \leqslant$ a.f $\leqslant 0.9$ the uncertainty in this parameter is judged to be $< \pm 0.05$, based on different runs with the same complex.

As mentioned above, the temperature at which the solid-state visible band at 540 nm appears is roughly the same as that at which the a.f. begins to depart from unity in the three complexes for which solid-state visible spectra were obtained. It was also seen in Table 2 that the intensity of this band increased very slightly with decreasing T for the nitrate derivative, somewhat more for the bromide, and quite strongly for the perchlorate monohydrate. The a.f. values indicate that these intensity changes are at least qualitatively related to the fraction of low-spin species present (1 — a.f).

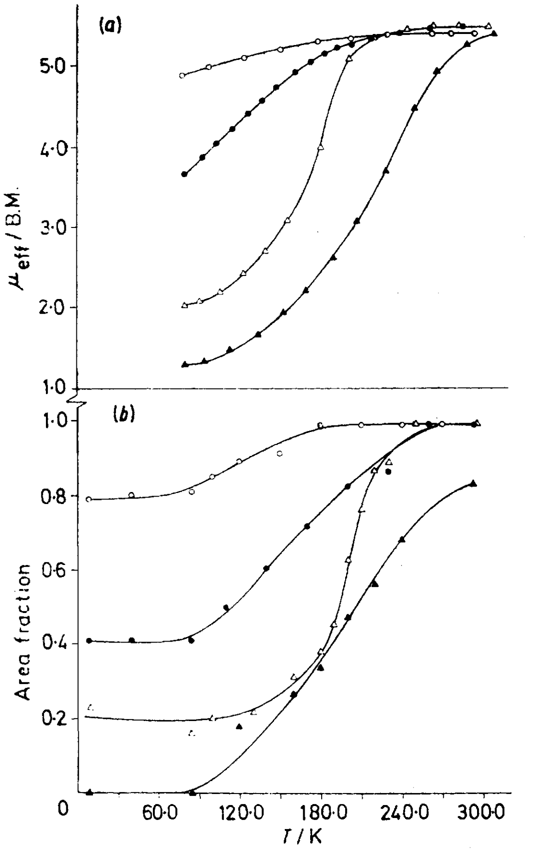


FIGURE 2 Temperature dependence of (a) the effective magnetic moments and (b) the Mössbauer area fractions of the complexes $[Fe(pbim)_3][ClO_4]_2{\cdot}2OH_2$ (▲), $[Fe(pbim)_3][ClO_4]_2{\cdot}OH_2$ (△), $[Fe(pbim)_3]Br_2$ (●), and $[Fe(pbim)_3][NO_3]_2{\cdot}OH_2$ (○)

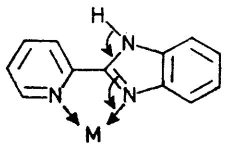
Although there is a clear qualitative correlation between $\mu_{eff.}$ and a.f. (Figure 2), there is no quantitative correlation as a few examples will illustrate. In the simplest possible approach one may assign a zero moment to the $^1A_{1g}$ state, a moment of *ca.* 5.4 B.M. to the $^5T_{2g}$ state, and then compute an ' average moment ' at a given temperature from the area fraction. This invariably leads to calculated moments much smaller than those observed. A further indication that this approach is incorrect is seen in the low-temperature data for the perchlorate dihydrate. This complex appears to be fully in the $^1A_{1g}$ state at liquid-nitrogen temperature, yet has a moment of *ca.* 1.3 B.M. at 80 K. Even if we assume that we cannot detect an a.f. value smaller than 0.1, the maximum moment obtained for this salt would be only *ca.* 0.5 B.M. on the basis of this procedure.

König and Kremer [23] discussed this problem in some detail. They pointed out that it is inappropriate to assign a moment of *ca.* 5.4 B.M. to the high-spin state due to the effects of spin–orbit coupling on the ground and excited states near the spin-crossover energy. There is also extensive mixing of eigenstates in this range of energies, which they suggested could lead to a non-zero moment for the low-spin state. Furthermore, the moments of both species vary as the energy difference ΔE between the two states changes. König and Kremer [23,24] postulated that in general ΔE changes with temperature in complexes showing spin crossover, implying that both the high- and low-spin fractions have temperature-dependent moments.

A very interesting feature of these data is that for $[Fe(pbim)_3][ClO_4]_2{\cdot}xOH_2$ both $\mu_{eff.}(T)$ and a.f.(T) change drastically when x changes from 1 to 2. It is clear from the ease with which the second lattice water molecule can be pumped off at room temperature that it is only loosely bound, whereas further dehydration of the complex cannot be achieved *in vacuo* even at 150 °C. There seem to be only two possible mechanisms by which the $^5T_{2g} : {}^1A_{1g}$ ratio could be affected by this second water molecule.

(1) *Crystal-packing effects.* König and Watson [5] showed that the Fe–N bonds in $[Fe(bipy)_2(NCS)_2]$ (bipy = 2,2′-bipyridyl) are slightly shorter in the low- than in the high-spin state. If the pbim complexes are similar in this respect it may be supposed that the additional water molecule produces a lattice compression effect which increases the low-spin fraction. However, Fisher and Drickamer [25] studied the effect of pressure on a number of phen and bipy complexes of Fe^{II}, and it appears from this work that pressures of the order of 10 kbar or more are required to produce a net conversion from high to low spin. It is almost inconceivable that this loosely held water molecule could cause an effect of this magnitude.

(2) *Hydrogen-bonding effects.* As mentioned above the imino-hydrogen atom on the benzimidazole portion of the pbim molecule is slightly acidic. The acidity increases on chelation,[13] and seems to bear a direct relation to the strength of the nitrogen–metal bond. This effect was attributed [13] to the resonance mechanism below. According to this scheme, the formation of a



stronger nitrogen–metal σ bond will enhance the acidity of the imino-hydrogen atom. To turn this argument

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[23] E. König and S. Kremer, *Theor. Chim. Acta*, 1971, **22**, 45.

[24] E. König and S. Kremer, *Theor. Chim. Acta*, 1971, **20**, 143.

[25] D. C. Fisher and H. G. Drickamer, *J. Chem. Phys.*, 1971, **54**, 4824.

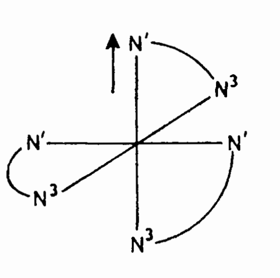
around, a weakening of the N–H bond by hydrogen bonding to a water molecule should cause a strengthening of the nitrogen–metal σ bond. In order to prevent too much charge accumulation on the metal, such an increase in N→M σ donation would probably be accompanied by an increase in back π donation from the metal t_{2g} orbitals to assist formation of the methine chromophore [22] characteristic of the low-spin state. These effects would be synergically related, since strengthening of the N–M σ bond and of the methine chromophore will both enhance the low-spin fraction.

Further support for the idea that hydrogen bonding plays an important role in the spin-crossover phenomenon in these cases is the fact that addition of trace quantities of strong protonic acids in the preparation of the complexes invariably increased the low-temperature magnetic moment. This is precisely the effect expected from the above argument, since the additional protons should decrease both the acidity of the imino-hydrogen atom and the strength of the N–Fe bond, and lead to a larger high-spin fraction. The energy of such an N–H · · · O hydrogen bond would presumably lie between those of an N–H · · · N bond (0.31 kJ mol^{-1} in NH_3) [26] and an N–H · · · F bond (1.20 kJ mol^{-1} in $[NH_4]F$).[26] These energies are typical of those encountered in physical adsorption systems such as the rare gases on graphite, where the adsorbed species can be readily pumped off,[27] and would account for the ease with which the dihydrate is converted into the monohydrate. However, the remaining water molecule is much more tightly held, but the way in which it is bound in the crystal lattice is not clear.

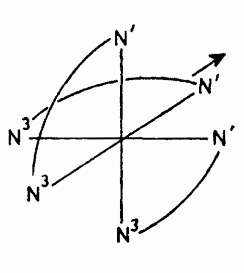
The Cation Structure.—In order to obtain more information on the electronic and geometrical structure of the $[Fe(pbim)_3]^{2+}$ cation in these complexes, Mössbauer spectra in longitudinal applied magnetic fields of 50 kG were obtained for two of the complexes. Such measurements enable one to determine the sign of V_{zz}, the principal component of the electronic-field-gradient (e.f.g) tensor, and the magnitude of the asymmetry parameter η $[\eta = (V_{xx} - V_{yy})/V_{zz}]$.

As pointed out above, for both the low- and high-spin species, isomer shift and quadrupole-splitting values show only a very slight dependence on the nature of the anion, suggesting that the basic structure of the cation in a given spin state is probably very similar in all four complexes. This suggestion is further supported by the fact that the i.r. spectra of the cations are identical throughout the series. For these reasons, and because of the difficulties in obtaining magnetic-perturbation spectra at high temperatures, only $[Fe(pbim)_3][ClO_4]_2 \cdot OH_2$ was studied by this technique at 295 K. The corresponding dihydrate is the only one of the four complexes which is fully low spin at 80 K and below, and was the other complex chosen for magnetic-perturbation studies. It should be noted that since the susceptibility is small at 295 K, the magnetization induced by the applied field is negligible. Under these conditions a paramagnetic complex will behave essentially like a diamagnetic one,[28,29] and the usual doublet–triplet spectrum [30] will obtain (provided $\eta \approx 0$). For high-spin $[Fe(pbim)_3][ClO_4]_2 \cdot OH_2$ at 295 K we find $V_{zz} > 0$ and $\eta = 0.5 \pm 0.1$. The applied-field spectrum of low-spin $[Fe(pbim)_3][ClO_4]_2 \cdot 2OH_2$ at 80 K is almost symmetrical showing that η is very close to unity, and the sign of V_{zz} cannot be determined unambiguously in this case.

The two nitrogen atoms of the pbim ligand which are bonded to iron are not equivalent. If we denote the pyridine nitrogen by N′ and the imidazole nitrogen by N^3, then the ligands can arrange themselves around the iron atom to give either a *mer*- or *fac*-octahedral structure. In the *mer*-octahedral form the symmetry about iron will be C_{2v} along the N′-Fe-N^3 direction, whilst in the *fac* form it is C_{3v} along the trigonal [1,1,1] axis of the octahedron. Due to the asymmetry of the ligand, steric requirements will favour the *mer*-octahedral form since in this case the three benzimidazole groups can be further apart than in the *fac*-octahedral structure.



mer



fac

The $^5T_{2g}$ ground state can be treated *via* the crystal-field model [31-33] described in detail elsewhere.[33] The *mer*-octahedral structure corresponds to a tetragonal distortion with the *z* axis of the e.f.g. along the N′-Fe-N^3 direction, and since the N′-Fe-N′ and N^3-Fe-N^3 axes are not equivalent there will be a substantial rhombic field as well. On the other hand, the *fac*-octahedral structure corresponds to a trigonal distortion and the rhombic term is expected to be small. The magnitude and temperature dependence of ΔE_Q for $[Fe(pbim)_3][ClO_4]_2 \cdot OH_2$ (Table 3) indicate that the ground state is an orbital singlet.[33] In the tetragonal case the singlet is $|xy>$, which will give $V_{zz} > 0$ as observed, in contrast to the trigonal case where the $|z^2>$ singlet will product a negative V_{zz}. A fit of the ΔE_Q and *T* data using the crystal-field model [33] yields a tetragonal distortion of −385 cm^{-1} and a rhombic splitting of −270 cm^{-1}. With these

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[27] J. R. Sams, *Progr. Surf. Membrane Sci.*, 1974, **8**, 1 and refs. therein.

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[31] R. Ingalls, *Phys. Rev.*, 1964, **133**, A787.

[32] T. C. Gibb, *J. Chem. Soc.* (*A*), 1968, 1439.

[33] J. R. Sams and T. B. Tsin, *Inorg. Chem.*, 1975, **14**, 1573.

crystal-field parameters the calculated η value is 0.45, in good agreement with the observed value. Thus, the Mössbauer data show conclusively that the cation in $[Fe(pbim)_3][ClO_4]_2{\cdot}OH_2$ adopts a *mer*-octahedral configuration, and there seems little reason to doubt that the other pbim complexes are similar. From the crystal-field treatment the spin–orbit coupling constant λ is estimated to be *ca.* 100 cm^{-1}. This indicates that there is no extensive delocalization of the t_{2g} electrons on to the ligands, consistent with an ' ionic ' $^5T_{2g}$ iron(II) system.

The low-spin ground state is more difficult to treat in a reasonably exact way. Both the σ- and π-bonding systems will contribute to the e.f.g.,[34,35] and the effects of these two contributions cannot be separately calculated. However, low-spin iron(II) complexes are expected to follow the point-charge model[36] fairly closely. This model predicts[37,38] $V_{xx} = V_{yy} = V_{zz} = 0$ for a *fac*-octahedral structure, and hence zero quadrupole splitting (although distortions from regular geometry could make $|\Delta E_Q| \neq 0$). For the *mer*-octahedral case the predictions are $V_{xx} = 0$ and $V_{yy} = -V_{zz}$, to give $\eta = 1$ and an indeterminate sign of the e.f.g. Thus, our results for low-spin $[Fe(pbim)_3][ClO_4]_2{\cdot}2OH_2$ are also fully consistent with a *mer*-octahedral structure.

It is interesting to compare these results with those obtained for $[Fe(2\text{-}Mephen)_3][BF_4]_2$ and $[Fe(2\text{-}Mephen)_3][ClO_4]_2$[9] (2-Mephen = 2-methyl-1,10-phenanthroline). In the $^5T_{2g}$ state the temperature dependence of $|\Delta E_Q|$ for these complexes suggests that the iron(II) ion has an orbital-singlet ground state, although in magnitude the splittings are considerably smaller than those of the pbim derivatives. This implies a smaller crystal-field distortion in the 2-Mephen complexes, which is probably due to the fact that the two nitrogen atoms in 2-Mephen are essentially equivalent, in contrast to the situation in pbim. This difference between the two types of ligands is even more clearly seen in the $^1A_{1g}$ states. In the 2-Mephen complexes V_{zz} is also positive, but η is close to zero, showing a quite symmetric environment about Fe^{II}.

Conclusions.—Our studies on the $[Fe(pbim)_3]^{2+}$ complexes have brought to light some interesting new features of the $^5T_{2g}$–$^1A_{1g}$ spin-crossover phenomenon. From solution and solid-state visible spectra we have been able to show that the crossover very probably occurs only in the solid state. This implies that the phenomenon depends not only on the field strengths of the ligands bonded to iron, but is ultimately controlled by crystalline forces in the lattice. That these forces are either weak or relatively remote from the iron(II) ion is demonstrated by the fact that large changes in Mössbauer area fraction from one complex to another are not accompanied by any significant changes in crystal-field splitting parameters (as indicated by ΔE_Q values for the high-spin fractions). As shown elsewhere,[33] these parameters are normally quite sensitive to small changes in the iron(II) environment. Accompanying the $^5T_{2g}$–$^1A_{1g}$ crossover in these complexes is the appearance of a strong visible absorption band, producing a dramatic colour change. This band has been interpreted as arising from the formation of a ' methine chromophore ' typical of covalent systems, and indicates that redistributions of both the iron(II) 3*d* electrons and the ligand π electrons are involved in the crossover process.

The influence of the hydration state of the crystal on the spin equilibrium has been attributed to hydrogen bonding between the water molecule and the acidic hydrogen on the benzimidazole fragment of the ligand. It seems likely that the different magnetic moments of $[Fe(pim)_3][SO_4]{\cdot}xOH_2$ for $x = 2$ and 3[12] are also due to hydrogen-bonding effects. The asymmetry of the pbim ligand allows in principle the existence of two geometrical isomers of the $[Fe(pbim)_3]^{2+}$ cation. Magnetic-perturbation Mössbauer spectra for both spin states indicate that it is the *meridional* isomer which occurs in these complexes.

EXPERIMENTAL

All chemicals were obtained from commercial sources and used without further purification. Since the iron(II) starting materials were air sensitive, the initial mixing of reagents in the preparation of the complexes was carried out under a dry nitrogen atmosphere. The ethanol referred to is 100% ethanol.

Tris[2-(2′-*pyridyl*)*benzimidazole*]*iron*(II) *Perchlorate Monohydrate*, $[Fe(pbim)_3][ClO_4]_2{\cdot}OH_2$.—A solution of $Fe[ClO_4]_2{\cdot}6OH_2$ (4.0 g) in ethanol (30 cm^3) was added to 2-(2′-pyridyl)-benzimidazole (6.5 g) dissolved in ethanol (200 cm^3). The complex precipitated after a few minutes, and was filtered off and washed with ethanol. The *product* was dried *in vacuo*. The crystals are orange at room temperature and purple at 80 K (Found: C, 50.4; H, 3.25; Fe, 6.50; N, 14.75. $C_{36}H_{29}Cl_2FeN_9O_9$ requires C, 50.35; H, 3.35; Fe, 6.50; N, 14.65%), Λ_M (1.16×10^{-3} mol dm^{-3}) 176 S cm^2 mol^{-1}.

Tris[2-(2′-*pyridyl*)*benzimidazole*]*iron*(II) *Perchlorate Dihydrate*, $[Fe(pbim)_3][ClO_4]_2{\cdot}2OH_2$.—Brown crystals of the *complex* were obtained when a sample of $[Fe(pbim)_3][ClO_4]_2{\cdot}OH_2$ was left to stand in air for 0.5 h. The compound is purple at 80 K (Found: C, 49.0; H, 3.50; Fe, 6.35; N, 14.4. $C_{36}H_{31}Cl_2FeN_9O_{10}$ requires C, 49.3; H, 3.55; Fe, 6.40; N, 14.4%), Λ_M(0.86×10^{-3} mol dm^{-3}) 188 S cm^2 mol^{-1}.

Tris[2-(2′-*pyridyl*)*benzimidazole*]*iron*(II) *Nitrate Monohydrate*, $[Fe(pbim)_3][NO_3]_2{\cdot}OH_2$.—To a solution of $[Fe(pbim)_3][ClO_4]_2{\cdot}OH_2$ (0.5 g) in methanol (200 cm^3) was added a large excess of $[NH_4][NO_3]$ dissolved in a minimum volume of water (*ca.* 30 cm^3). The resulting solution was concentrated under reduced pressure to a volume of *ca.* 60 cm^3 and left to stand overnight. The red-orange crystals which formed were washed with water and recrystallized from cold methanol to yield the pure *product*, which was dried

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in vacuo (Found: C, 54.6; H, 3.65; Fe, 7.15; N, 19.7. $C_{36}H_{29}FeN_{11}O_7$ requires C, 55.2; H, 3.70; Fe, 7.15; N, 19.7%), $\Lambda_M(0.94 \times 10^{-3}$ mol dm$^{-3}) = 165$ S cm^2 mol^{-1}. The *product* is purple at 80 K.

Tris[2-(2′-*pyridyl*)*benzimidazole*]*iron*(II) *Bromide*, [Fe(pbim)$_3$]Br$_2$.—To a solution of anhydrous iron(II) bromide (0.8 g) in ethanol (30 cm^3) was added a solution of the ligand (2.4 g) in the same solvent at room temperature. The resulting deep red solution was filtered, concentrated to half volume under reduced pressure, and left to stand overnight. The orange crystals of the *complex* were collected, washed with ethanol, and dried *in vacuo*. The colour of the compound is purple at 80 K (Found: C, 53.4; H, 3.40; Fe, 6.95; N, 15.8. $C_{36}H_{27}Br_2FeN_9$ requires C, 53.9; H, 3.35; Fe, 6.95; N, 15.7%), $\Lambda_M(0.82 \times 10^{-3}$ mol dm$^{-3}) = 160$ S cm^2 mol^{-1}.

Microanalyses for C, H, and N were by P. Borda of this Department and by Drs. F. and E. Pascher, Mikroanalytical Laboratorium, Bonn, West Germany. Iron analyses were made with a Perkin-Elmer 305A atomic-absorption spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer in the range 250—4000 cm^{-1}. The solid samples were used either as Nujol mulls between CsI plates or as KBr pellets. Molar conductances in methanol were determined at 25 °C using an A.C. conductance bridge set at a frequency of 1 000 Hz. Magnetic susceptibilities were obtained with a variable-temperature Gouy balance over the range 80—310 K. All measurements were made at two field strengths, and no field dependence was observed. The apparatus was calibrated with mercury(II) tetrathiocyanatocobaltate(II), and Pascal's constants were used to correct for diamagnetism. Electronic spectra were recorded on a Cary model 14 instrument; KBr pellets were used for solid samples, and solution spectra were obtained in 1 cm standard quartz optical cells. Data at low temperatures were obtained in a brass Dewar vessel fitted with glass windows. Temperature variation was achieved by passing controlled amounts of cold N_2 vapour into the inner chamber of the Dewar, and temperatures were measured with a copper–constantan thermocouple. The Mössbauer spectrometer and attendant experimental details have been described previously.[33,39,40] Spectra obtained in the absence of an applied magnetic field were least-squares fitted to Lorentzian components,[39] and isomer shifts are quoted relative to the centroid of the disodium pentacyanonitrosylferrate(II) dihydrate spectrum. Theoretical magnetic perturbation spectra used for comparison with the experimental spectra were generated by a program kindly supplied by Dr. G. Lang.[41]

We are grateful to Professor J. B. Farmer for the use of the atomic-absorption spectrophotometer, Professor G. B. Porter for the loan of his low-temperature visible spectral cell, Dr. R. C. Thompson for the use of the Gouy balance and A. C. conductance bridge, Mrs. A. Sallos for valuable technical assistance, and the National Research Council of Canada for support and the award of a postgraduate scholarship (to T. B. T.).

[5/1061 *Received*, 2*nd June*, 1975]

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