3438 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3438—3442 (1973) [Vol. 46, No. 11

The Magnetic Properties of Iron(II) Complexes with 2-(2'-Pyridyl)imidazole and Its Derivatives

Yoshihiro Sasaki and Tsunenobu Shigematsu

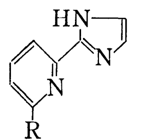
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

(Received May 14, 1973)

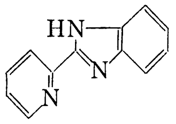
The magnetic susceptibilities and Mössbauer spectra of iron(II) complexes of 2-(2'-pyridyl)imidazole (PI), 2-(6'-methyl-2'-pyridyl)imidazole (6-MPI), and 2-(2'-pyridyl)benzimidazole (PBI) have been measured in the 4.2—298 K temperature range. The results show that $Fe(II)(PI)_3(ClO_4)_2H_2O$ and $Fe(II)(PBI)_3(ClO_4)_2H_2O$ have a spin equilibrium between $^1A_1$ and $^5T_2$, while $Fe(II)(6\text{-}MPI)_3(ClO_4)_2H_2O$ does not have such an equilibrium. The temperature dependence and magnitude of the magnetic data for $Fe(II)(PBI)_3(ClO_4)_2H_2O$ and $Fe(II)(6\text{-}MPI)_3(ClO_4)_2H_2O$ have been calculated by using a parametric ligand-field approximation. The results indicate that the orbital splittings of the $^5T_2$ ground state due to trigonal distortion are -2000 and $-800\ \mathrm{cm}^{-1}$ for $Fe(II)(6\text{-}MPI)_3(ClO_4)_2H_2O$ and $Fe(II)(PBI)_3(ClO_4)_2H_2O$ respectively.

Transition-metal octahedral complexes with the electronic configuration d^6 may exist in either one of two different electronic ground states, $^5T_2$ (high-spin $t_2{}^4e^2$) and $^1A_1$ (low-spin $t_2{}^6$). Under special circumstances, the energy difference between these two states at a certain temperature may become comparable to the thermal energy, kT. If, at a field strength, Δ, close to the mean spin-pairing energy, π, the separation of the two states attains a value within the thermally-accessible range, an equilibrium between the $^1A_1$ and $^5T_2$ states can be expected to occur. Orgel has suggested that the diamagnetism of tris(1,10-phenanthroline)iron(II) complexes can not be expected from simple ligand-field calculations in which $\Delta<\pi$ (Fe^{2+}; $17600\ \mathrm{cm}^{-1}$).[1] The complex formation must, therefore, produce a marked decrease in π from the estimated free ion value. Thus, iron(II) complexes with α-diimine chelate rings appear to be close to a $^5T_2$–$^1A_1$ crossover system. Certain iron(II) complexes of 2-(2'-pyridyl)imidazole, 2-(2'-pyridyl)imidazoline and 2-methyl-1,10-phenanthroline, exhibit anomalous magnetic behavior indicative of the $^5T_2$–$^1A_1$ crossover.[2–6]

We have prepared iron(II) octahedral complexes with 2-(6'-methyl-2'-pyridyl)imidazole (I, R=CH_3; 6-MPI) and 2-(2'-pyridyl)benzimidazole (II; PBI); the variations in their magnetic susceptibilities and Mössbauer spectra with the temperature will be reported in this paper. Moreover, we have re-examined an iron complex with 2-(2'-pyridyl)imidazole (I, R=H; PI) and will report the results here.



I



II

Experimental

Preparation of the Reagents. (*a*) *2-(2'-Pyridyl)imidazole.* A procedure similar to that described by Chiswell *et al.* was used[7] except that, after extracting 2-(2'-pyridyl)imidazole many times with ether, the solvent was removed from the combined, dried ether extracts and the residual oil was sublimated *in vacuo* twice. Pale yellow crystals were collected and recrystallized from ethyl acetate as white crystals; mp 134.5—135 °C.

(*b*) *2-(6'-Methyl-2'-pyridyl)imidazole.* This reagent was prepared similarly from 6-methylpyridine-2-aldehyde; white crystals, mp 169 °C.

(*c*) *2-(2'-Pyridyl)benzimidazole.* A procedure similar to that described by Walter and Freiser was used.[8] α-Picolinic acid and *o*-phenylenediamine were allowed to react with each other at 170—180 °C for 3 hr. The product was crystallized from ethanol-water solution as red-violet crystals and was then sublimed. The recrystallization of the sublimate from ethyl acetate, followed by sublimation, yielded white crystals of 2-(2'-pyridyl)benzimidazole; mp 220 °C.

Preparation of Complexes. All preparations were carried out in a nitrogen atmosphere using air-free water and ethanol. All the complexes were dried *in vacuo* over silica gel at room temperature.

(*a*) *Tris-[2-(2'-pyridyl)imidazole] Iron(II) Perchlorate Monohydrate.* Solutions of 2-(2'-pyridyl)imidazole (2.2 g) in ethanol (10 ml) and ferrous perchlorate hexahydrate (1.8 g) in water (10 ml) were mixed. The dark red solution thus formed was concentrated to half-volume under reduced pressure; the complex was then precipitated on cooling. When it was recrystallized from 1 : 1 ethanol-water, dark red crystals were obtained. Found: C, 40.50; H, 3.29; N, 17.33; Fe, 7.90%. Calcd for $FeC_{24}H_{23}N_9O_9Cl_2$: C, 40.69; H, 3.27; N, 17.80; Fe, 7.88%.

(*b*) *Tris-[2-(6'-methyl-2'-pyridyl)imidazole] Iron(II) Perchlorate Monohydrate.* This complex was prepared similarly from 2-(6'-methyl-2'-pyridyl)imidazole; yellow crystals. Found: C, 42.67; H, 3.76; N, 16.80; Fe, 7.34%. Calcd for $FeC_{27}H_{29}N_9O_9Cl_2$: C, 43.22; H, 3.90; N, 16.80; Fe, 7.44%.

(*c*) *Tris-[2-(2'-pyridyl)benzimidazole] Iron(II) Perchlorate Monohydrate.* Solutions of 2-(2'-pyridyl)benzimidazole (2.9 g) and ferrous chloride tetrahydrate (1.0 g) in minimum quantities of ethanol were mixed. Perchloric acid (2.2 ml

---

1) L. E. Orgel, Report of the 10th Solvay Conference in Chemistry, Brussels, 1956, p. 289.

2) D. M. L. Goodgame and A. A. S. C. Machado, *Inorg. Chem.*, **8**, 2031 (1969).

3) R. L. Dosser, W. J. Eilbeck, A. E. Underhill, P. R. Edwards, and C. E. Johnson, *J. Chem. Soc., A*, **1969**, 810.

4) D. M. L. Goodgame and A. A. S. C. Machado, *Chem. Commun.*, **1969**, 1420.

5) H. A. Goodwin and R. N. Sylva, *Aust. J. Chem.*, **21**, 83 (1968).

6) E. König, G. Ritter, H. Spiering, S. Kremer, K. Madeja, and A. Rosenkranz, *J. Chem. Phys.*, **56**, 3139 (1972).

7) B. Chiswell, F. Lions, and B. S. Morris, *Inorg. Chem.*, **3**, 110 (1964).

8) J. L. Walter and H. Freiser, *Anal. Chem.*, **26**, 217 (1954).

of 70% aqueous solution) and water were then added, and reddish-brown crystals were precipitated. Found: C, 50.02; H, 3.31; N, 14.41; Fe, 6.65%. Calcd for $FeC_{36}H_{29}N_9O_9Cl_2$: C, 50.37; H, 3.41; N, 14.69; Fe, 6.51%.

Magnetic Measurements. Magnetic susceptibilities were measured using a torsion balance magnetometer. The molar susceptibilities were corrected for diamagnetism, using the following corrections: Fe^{2+}, −13; H_2O, −13; ClO_4^-, −32; 2-(2′-pyridyl)imidazole, −82; 2-(2′-pyridyl)benzimidazole, −118; 2-(6′-methyl-2′-pyridyl)imidazole, −97 (in units of 10^{-6} cgs/mol). The effective magnetic moment, μ_{eff}, was obtained from the relation: $\mu_{eff}=2.828\sqrt{\chi'_M T}$, χ_M' being the fully corrected molar susceptibility, and T, the temperature in K.

Mössbauer Effect Measurements. The Mössbauer spectra were obtained with a scanning velocity spectrometer in the time mode. The radiation source was ^{57}Co diffused into a copper foil and kept at room temperature during all measurements. The velocity scale was calibrated with metallic iron, and the velocity was determined to an accuracy of ±0.04 mm/s.

Electronic Spectra. The electronic spectra of these complexes were measured with a Hitachi 323 automatic recording spectrophotometer.

Results and Discussion

Magnetic Data. The results of magnetic susceptibility measurements of polycrystalline samples between 77 and 298 K are listed in Table 1, while the variation in μ_{eff} with the temperature is shown in Fig. 1. The magnetic-moment values for Fe(II)(6-MPI)$_3$(ClO$_4$)$_2$H$_2$O are characteristic of an iron(II) ion in a $^5T_2$ ground state. Within the 77—298 K temperature range, the susceptibility follows the Curie-Weiss law: $\chi'_M=C/(T-\Theta)$; the resulting value of the Weiss constant, Θ, is −3°.

The magnetic-moment values for the other complexes indicate that these compounds possess anomalous magnetic properties. The values of susceptibility for Fe(II)(PI)$_3$(ClO$_4$)$_2$H$_2$O are in agreement with those reported by Goodgame and Machado.[2] The temperature dependence of the Curie-Weiss plot for Fe(II)(PBI)$_3$(ClO$_4$)$_2$H$_2$O is shown in Fig. 2. This plot exhibits that, within the 220.5—298 K temperature range, the susceptibility follows the Curie-Weiss law and that the value of the Weiss constant, Θ, is −2°.

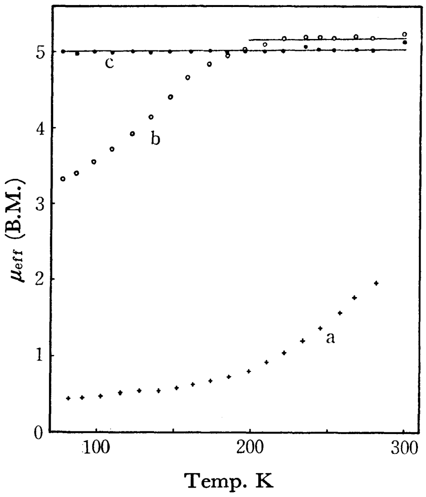


Fig. 1. Temperature dependence of the effective magnetic moments.
a: Fe(II)(PI)$_3$(ClO$_4$)$_2$H$_2$O, b: Fe(II)(PBI)$_3$(ClO$_4$)$_2$-H$_2$O, c: Fe(II)(6-MPI)$_3$(ClO$_4$)$_2$H$_2$O.
The solid lines are calculated theoretically with the parameters, $v'=0$ cm^{-1}, $\lambda=-80$ cm^{-1}, $\kappa=0.8$ and $v=-800$ and -2000 cm^{-1} for Fe(II)(PBI)$_3$(ClO$_4$)$_2$H$_2$O and Fe(II)(6-MPI)$_3$(ClO$_4$)$_2$H$_2$O, respectively.

The increase in χ'_M with a rise in the temperature

TABLE 1. MAGNETIC DATA FOR Fe(II)(PI)$_3$(ClO$_4$)$_2$H$_2$O, Fe(II)(PBI)$_3$(ClO$_4$)$_2$H$_2$O AND Fe(II)(6-MPI)$_3$(ClO$_4$)$_2$H$_2$O

Fe(II)(PI)$_3$(ClO$_4$)$_2$H$_2$O			Fe(II)(PBI)$_3$(ClO$_4$)$_2$H$_2$O			Fe(II)(6-MPI)$_3$(ClO$_4$)$_2$H$_2$O		
T(K)	$10^6\chi'_M$ (cgs/mol)	μ_{eff} (B.M.)	T(K)	$10^6\chi'_M$ (cgs/mol)	μ_{eff} (B.M.)	T(K)	$10^6\chi'_M$ (cgs/mol)	μ_{eff} (B.M.)
281.8	1668	1.94	298.0	11554	5.25	298.0	11101	5.14
267.1	1426	1.75	278.1	12157	5.20	278.1	11392	5.03
258.1	1159	1.55	267.5	12761	5.22	267.5	11807	5.03
244.7	917	1.34	253.3	13314	5.19	253.3	12429	5.02
233.3	748	1.18	243.7	13917	5.21	243.7	13052	5.04
221.3	602	1.03	234.7	14420	5.20	234.7	13757	5.08
210.3	481	0.90	220.5	15224	5.18	220.5	14255	5.01
199.1	384	0.78	207.8	15626	5.10	207.8	15210	5.03
186.6	336	0.71	195.1	16279	5.04	195.1	16081	5.01
174.6	312	0.66	183.8	16782	4.97	183.8	16953	4.99
163.0	288	0.61	172.5	17084	4.85	172.5	18323	5.03
152.1	263	0.57	159.4	17084	4.67	159.4	19651	5.01
139.9	239	0.52	146.4	16732	4.43	146.4	21269	4.99
127.7	263	0.52	133.9	16078	4.15	133.9	23386	5.00
115.6	263	0.49	122.1	15777	3.93	122.1	25710	5.01
102.6	263	0.46	109.2	15777	3.71	109.2	28490	4.99
90.4	239	0.42	97.2	16330	3.56	97.2	32018	4.99
82.8	263	0.42	85.9	16883	3.41	85.9	35961	4.97
			77.2	17989	3.33	77.2	40277	4.99

seems to be caused by either an antiferromagnetic interaction between iron(II) ions or by a thermal equilibrium involving terms of different spin multiplicities. Since all the complexes contain three ligand molecules around a central ion and since the Weiss constants of the complexes are small, it seems unlikely that an iron-iron antiferromagnetic interaction occurs in these compounds. Therefore, the most plausible explanation is that there is an equilibrium between two different spin states. Octahedral iron(II) complexes may exist in either the $^5T_2$ or the $^1A_1$ ground state, and the energy separation between these two states may become comparable to the thermal energy, kT, under special circumstances.[9] Thus, we suggest that the observed results can be explained in terms of a spin equilibrium involving $^5T_2$ and $^1A_1$ electronic states.

TABLE 2. MÖSSBAUER PARAMETERS δ^{IS} AND ΔE_Q (in mm/s)

Compound	Temp. (K)	δ^{IS} (S=0)	ΔE_Q (S=0)	δ^{IS} (S=2)	ΔE_Q (S=2)	Ratio of peak intensity a_h/a_l
$Fe(II)(PI)_3(ClO_4)_2H_2O$	298	0.40	0.40	—	—	
$Fe(II)(PBI)_3(ClO_4)_2H_2O$	298	—	—	0.96	1.99	
	77.2	0.47	0.40	0.98	2.27	0.63
	4.2	0.50	0.46	1.11	2.47	0.61
$Fe(II)(6\text{-}MPI)_3(ClO_4)_2H_2O$	298	—	—	1.03	2.09	
	100	—	—	1.13	2.43	
	77.2	—	—	1.13	2.43	

error = ±0.04 mm/s.

Mössbauer Spectra. The Mössbauer effect can be readily distinguished between the low- and high-spin forms of iron(II).[10] Characteristically S=0 Fe^{II} ions have an isomer shift, δ^{IS}, in the −0.1—+0.4 mm/s range with respect to iron, and have a quadrupole splitting, ΔE_Q, which is strongly dependent on coordination, 0.0—1.0 mm/s. For S=2 Fe^{2+} ions, δ^{IS} is in the 0.9—1.6 mm/s range and ΔE_Q, in the 1.2—3.5 mm/s range. The values of the Mössbauer parameters for the present complexes are listed in Table 2. These parameters were computed by fitting the data to the Lorentzian by means of a least-squares computer program. The Mössbauer spectra of $Fe(II)(PBI)_3(ClO_4)_2H_2O$ at 298, 77.2, and 4.2 K are shown in Fig. 3.

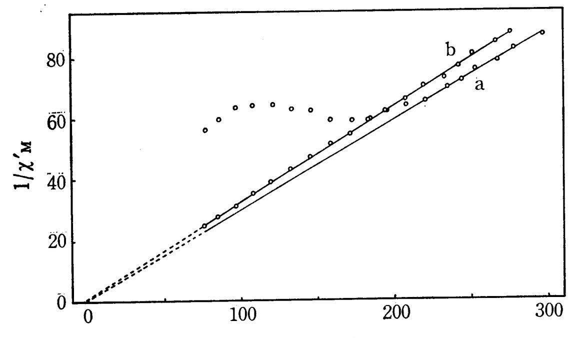


Fig. 2. Plots of resiprocal molar susceptibilities against absolute temperature.
a: $Fe(II)(PBI)_3(ClO_4)_2H_2O$, b: $Fe(II)(6\text{-}MPI)_3(ClO_4)_2H_2O$.

The spectra of $Fe(II)(6\text{-}MPI)_3(ClO_4)_2H_2O$ at 298, *ca.* 100, and 77.2 K consist of a doublet expected for the S=2 Fe^{2+} ion, which has a distortion, leaving an orbital singlet as the ground state. The spectrum of $Fe(II)(PI)_3(ClO_4)_2H_2O$ at 298 K, on the other hand, consists of a doublet due to the low-spin isomer, and the resonance lines due to the high-spin isomer cannot be observed because of the lower relative concentration of the high-spin form. The spectrum of $Fe(II)(PBI)_3(ClO_4)_2H_2O$ at 298 K consists of a doublet centered at 0.96 mm/s, with a quadrupole splitting of 1.99 mm/s, and the spectra at 77.2 and 4.2 K change into two doublets. We attribute the outer peaks to Fe^{2+} in the S=2 state, and inner pair, to Fe^{II} in the S=0 state.

TABLE 3. ABSORPTION MAXIMA IN THE ELECTRONIC SPECTRA

Compound	d-d Band (log ε) (cm⁻¹)	CT band (log ε) (cm⁻¹)
$Fe(II)(PI)_3(ClO_4)_2H_2O$	—	25100 20500
$Fe(II)(PBI)_3(ClO_4)_2H_2O$	—	20400
$Fe(II)(6\text{-}MPI)_3(ClO_4)_2H_2O$	11900 (0.91) 8600 (0.83)	26200 (2.78)

Electronic Spectra. The band maxima in the electronic spectra measured in ethanol are listed in Table 3. The molar extinction coefficients of $Fe(II)(PI)_3(ClO_4)_2H_2O$ and $Fe(II)(PBI)_3(ClO_4)_2H_2O$ vary with their concentrations. The electronic spectrum of $Fe(II)(6\text{-}MPI)_3(ClO_4)_2H_2O$ is characteristic of a high-spin complex whose d-d band splits into two components. The average of the band energies may be taken as a rough estimate of the ligand-field splitting, Δ. In this way, we obtained $\Delta \simeq 10300\ cm^{-1}$ for $Fe(II)(6\text{-}MPI)_3(ClO_4)_2H_2O$.

Calculation of the Ligand-field Parameters. We carried out a ligand-field calculation for d^6 quintet states, including the spin-orbit coupling and the trigonal component in the ligand field. Since we worked within a ^5D state, this calculation does not include the singlet state in the spin equilibrium.

The predominant cubic field splits the atomic ^5D term into $^5T_2$ and appriximately 10000 cm⁻¹-higher-lying ^5E. The ligand-field splitting parameter, Δ, for $Fe(II)(6\text{-}MPI)_3(ClO_4)_2H_2O$ is 10300 cm⁻¹. The trigonal distortion splits the $^5T_2$ ground term into ^5E and $^5A_1$, and the separation between these terms is called δ. Whenever the orbital doublet, ^5E, is the lowest, the sign of δ can be chosen as positive, and *vice versa.* If the z axis is taken along the (1,1,1) direction of the octahedron, the trigonal potential, V_t, has the form:

$$Ar^2C_0^{(2)}(\theta,\varphi) + Br^4[C_0^{(4)}(\theta,\varphi) - 1/2\sqrt{7/10}(C_3^{(4)}(\theta,\varphi) - C_{-3}^{(4)}(\theta,\varphi))] \qquad (1)$$

---

[9] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 776 (1954).

[10] J. F. Duncan and R. M. Golding, *Quart. Rev.*, **19**, 36 (1965).

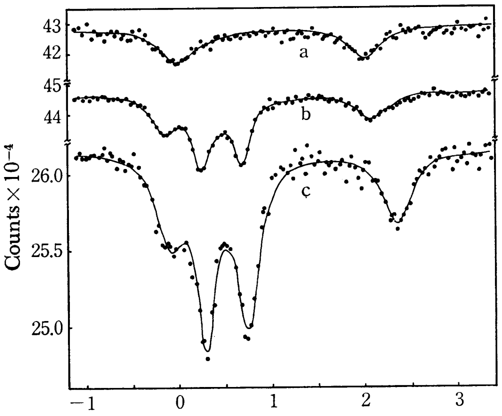


Fig. 3. Mössbauer spectra of $Fe(II)(PBI)_3(ClO_4)_2H_2O$.
a: 298 K, b: 77.2 K, c: 4.2 K.

where $C^{(k)}_{m}(\theta,\varphi)=(4\pi/(2k+1))^{1/2}Y_{km}(\theta,\varphi)$. δ is calculated by using the parameters, v and v', of Pryce and Runciman.[11] Their parameters are related to the parameters in Eq. (1) in the following way:

$$\overline{Ar^2} = v - 2\sqrt{2}\,v'$$

$$\overline{Br^4} = \frac{4}{3}v + 2\sqrt{2}\,v'. \tag{2}$$

Since $\delta \ll \Delta$ in general, δ depends almost entirely on the value of v and is not sensitive to v'. Thus, v' is assumed to be zero throughout the discussion.

The matrix elements of the Hamiltonian:

$$\boldsymbol{H} = V_t - \lambda \boldsymbol{L}\cdot\boldsymbol{S} \tag{3}$$

were evaluated within the 15 states $|M_L M_S\rangle$ of a $^5T_2$ term classified according to their M_J values. The eigenvalues and eigenfunctions generated in this calculation may be used to evaluate the magnitude and temperature dependence of the effective magnetic moment of a high-spin ferrous system.

The usual Van Vleck formulation is used for the magnetic susceptibility. It has to be calculated separately in both the direction parallel to and that perpendicular to the principal axis. The average magnetic susceptibility, $\bar{\chi}$, may be obtained from the principal magnetic susceptibilities, $\chi_{/\!/}$ and $\chi_{\perp}$ according to:

$$\bar{\chi} = \frac{1}{3}(\chi_{/\!/}+2\chi_{\perp}). \tag{4}$$

Then, the average magnetic moment, $\bar{\mu}$, was determined by $\bar{\chi}$ as a function of parameters, v and λ, and the orbital reduction factor κ.

The curves of the average magnetic moment against the temperature for various values of v are shown in Figs. 4 and 5. It can be seen that the temperature dependence of the magnetic moment for a positive v value is qualitatively different from that for a large negative v value. For a positive v value, there is a maximum in the curve, while for a large negative v value, the curve is essentially flat down to ~15 K. Taking account of the covalency effects, we fixed $\lambda=-80\ \mathrm{cm^{-1}}$ and $\kappa=0.8$. Thus, the value of δ can be easily determined by the curve-fitting method. The solid lines for $Fe(II)(6\text{-}MPI)_3(ClO_4)_2H_2O$ and $Fe(II)(PBI)_3(ClO_4)_2H_2O$ in Fig. 1 were calculated for $v=-2000$ and $-800\ \mathrm{cm^{-1}}$ respectively. It is immdeiately clear from Fig. 1 that v is negative, giving an orbital singlet as the ground state, and that $\delta \simeq -2000$ and $-800\ \mathrm{cm^{-1}}$ for $Fe(II)(6\text{-}MPI)_3(ClO_4)_2H_2O$ and $Fe(II)(PBI)_3(ClO_4)_2H_2O$. The quadrupole splitting in the Mössbauer spectra of $Fe(II)(PI)_3(ClO_4)_2H_2O$ and $Fe(II)(PBI)_3(ClO_4)_2H_2O$ in S=0 arises from this trigonal distortion. It has been reported that $Fe(II)(bipy)_3(ClO_4)_2$, which is in a low-spin form, exhibits a similar quadrupole splitting.[12] Therefore, this complex probably has a large trigonal distortion.

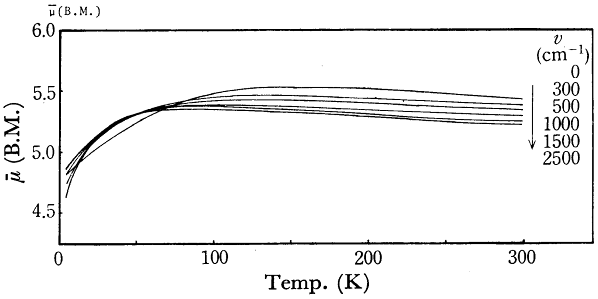


Fig. 4. Temperature dependence of the average magnetic moment of a high-spin ferrous complex as a function of trigonal distortion for positive values of v.
$\lambda=-80\ \mathrm{cm^{-1}}$, $\kappa=0.8$.

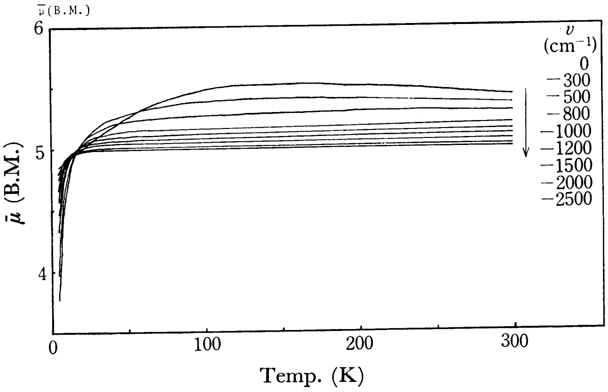


Fig. 5. Temperature dependence of the average magnetic moment of a high-spin ferrous complex as a function of trigonal distortion for negative values of v.
$\lambda=-80\ \mathrm{cm^{-1}}$, $\kappa=0.8$.

Two approaches have been previously employed to interpret the crossover system qualitatively. The first is the calculation of the temperature dependence of the susceptibility in terms of the Boltzmann distribution between $^5T_2$ and $^1A_1$ states separated from each other by a fixed energy, ΔE.[13] However, this method is not successful in the present case. The second approach is an empirical one in which one calculates an equilibrium constant in terms of the relative concentrations of the high- and low-spin forms.[1,14] We define the equilibrium constant as $K=[HS]/[LS]$, which is cal-

---

[11] M. H. L. Pryce and W. A. Runciman, *Discuss. Faraday Soc.*, **26**, 34 (1958).

[12] R. L. Collins, R. Pettit, and W. A. Baker, Jr., *J. Inorg. Nucl. Chem.*, **28**, 1001 (1966).

[13] B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York (1966).

[14] R. G. Stoufer, D. W. Smith, E. A. Clevenger, and T. E. Norris, *Inorg. Chem.*, **5**, 1167 (1966).

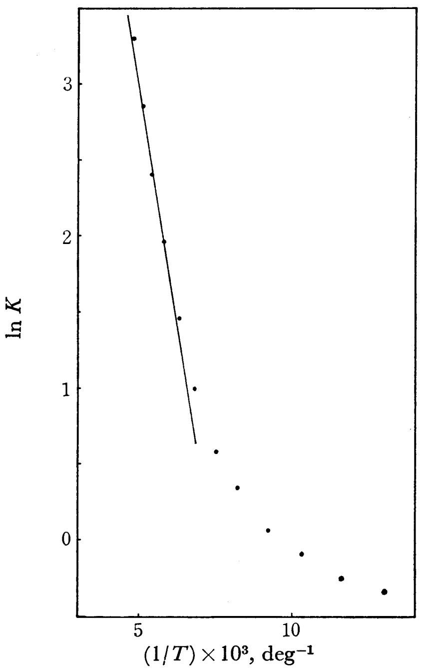


Fig. 6. Plot of ln$K$ for Fe(II)(PBI)$_3$(ClO$_4$)$_2$H$_2$O against $1/T$.

culated easily from the observed results. In order to calculate K, it is assumed that the susceptibility of the $^5T_2$ state follows the Curie-Weiss law within the temperature range of 77—298 K and that the temperature-independent paramagnetism for the $^1A_1$ state is 50×10^{-6} cgs/mol.[13] According to this assumption, the K value of Fe(II)(PBI)$_3$(ClO$_4$)$_2$H$_2$O at 77.2 K is 0.71. Figure 6 shows the temperature dependence of ln$K$ as calculated from the experimental susceptibility of Fe(II)(PBI)$_3$(ClO$_4$)$_2$H$_2$O. The curvature of the ln$K$ against $1/T$ plot reveals that this method is inadequate over the full temperature range. However, ΔH is essentially constant over the 159.4—207.8 K range and is listed in Table 4, along with the ΔS calculated there. Assuming that the Weiss constant is $-2°$ and that $\chi'_M=11000\times10^{-6}$ cgs/mol at 298 K (these represent typical experimental values for such species), one can plot ln$K$ against $1/T$ and calculate ΔH and ΔS for Fe(II)(PI)$_3$(ClO$_4$)$_2$H$_2$O (Table 4).

Table 4. Thermodynamic parameters for spin equilibrium

Compound	Temperature range (K)	ΔH (kcal/mol)	ΔS (e.u.)
Fe(II)(PBI)$_3$(ClO$_4$)$_2$H$_2$O	159.4—207.8	2.49	18.43
Fe(II)(PI)$_3$(ClO$_4$)$_2$H$_2$O	210.3—281.8	2.96	6.89

The entropy change for a simple spin equilibrium between singlet and quintet states may be only 3.2 eu. Since the ΔS values in the $^5T_2$–$^1A_1$ equilibria of these complexes are larger than 3.2 eu, it appears that additional factors, such as changes in the bond length and/or lattice spacing, play an important role in deciding the details of the temperature variation in the magnetic susceptibilities.

We can also obtain the relative concentrations of the low- and high-spin forms in Fe(II)(PBI)$_3$(ClO$_4$)$_2$H$_2$O from the Mössbauer spectra if the recoilless fractions are same for the two states (it is not likely that they are very different). Then, the equilibrium constant, K, is 0.63 at 77.2 K and 0.61 at 4.2 K. The results indicate that *ca.* 40% of the molecules are permanently in a $^5T_2$ state. According to the model for a spin equilibrium between $^5T_2$ and $^1A_1$ suggested by Bari and Sivardière, all the molecules should exist in a $^1A_1$ state at a considerably low temperature.[15] Therefore, we suggest that two chemical species may co-exist, one exhibiting a spin equilibrium and the other existing in a $^5T_2$ state. The asymmetry of 2-(2′-pyridyl)-benzimidazole as a chelating ligand allows, in theory, the formation of *vicinal* and *meridional* geometric isomers. Then, such geometric isomerism may result in the formation of two isomers possessing some different magnetic properties.

Recently a report about the magnetic behavior of some iron(II) complexes containing 2-(2′-pyridyl)benzimidazole was published.[16] The results indicate the existence of a $^5T_2$–$^1A_1$ spin equilibrium, but the details are not consistent with our investigation because these samples are different from the present complex.

Conclusion

The temperature dependence of the magnetic moments of Fe(II)(PI)$_3$(ClO$_4$)$_2$H$_2$O and Fe(II)(PBI)$_3$(ClO$_4$)$_2$H$_2$O indicate the presence of a spin equilibrium between the $^5T_2$ and $^1A_1$ states. The results of the Mössbauer spectra of Fe(II)(PBI)$_3$(ClO$_4$)$_2$H$_2$O are consistent with the existence of such a spin equilibrium. This behavior is in marked contrast to that of Fe(II)(6-MPI)$_3$(ClO$_4$)$_2$H$_2$O, which is a high-spin complex within the temperature range of 77—298 K. The difference in the magnetism of these complexes arises from the steric hindrance introduced by the 6′-methyl group.

The temperature dependence and magnitude of the magnetic moments of Fe(II)(PBI)$_3$(ClO$_4$)$_2$H$_2$O and Fe(II)(6-MPI)$_3$(ClO$_4$)$_2$H$_2$O existing in a $^5T_2$ state can be reproduced well using the parametric ligand-field theory. The results indicate that the orbital splittings of the $^5T_2$ state due to trigonal distortion are -2000 and -800 cm^{-1} for Fe(II)(6-MPI)$_3$(ClO$_4$)$_2$H$_2$O and Fe(II)(PBI)$_3$(ClO$_4$)$_2$H$_2$O respectively.

The authors wish to thank Dr. T. Shinjo and Mr. T. Matsuzawa for permitting us to use equipments for Mössbauer and magnetic measurements, respectively and for their helpful discussions.

---

[15] R. A. Bari and J. Sivardière, *Phys. Rev.*, **B 5**, 4466 (1972).

[16] J. R. Sams, J. C. Scott, and T. B. Tsin, *Chem. Phys. Lett.*, **18**, 451 (1973).