Spin-crossover behaviour of iron(III) complexes with pendant type polymeric ligands

Yonezo Maeda*, Makoto Miyamoto, Yoshimasa Takashima
Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashiku, Fukuoka 812 (Japan)
and Hiroki Oshio
Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Aramaki, Sendai 980 (Japan)

(Received April 7, 1992; revised October 5, 1992)

Abstract

Pendant type polymeric iron(III) complexes [FeL^{1}P]X, [FeL^2]X or [FeL^{3}P]X (where P = polymeric-4-vinylpyridine (pvp), copolymer of octylmetacrylate and 4-vinylpyridine (pomp), or copolymer of octylmetacrylate and 1-vinylimidazole (pomi); H_2L^1 = copolymeric Schiff base of 5,5′-methylene-bis-salicylaldehyde and dipropylenetriamine (psalten); H_2L^2 = copolymeric Schiff base of 5,5′-methylene-bis-salicylaldehyde and triethylenetetramine (psal$_2$trien); H_2L^3 = Schiff base prepared by condensation of salicylaldehyde and triethylenetetramine (H_2salten), X = tetraphenylborate ion (BPh_4^-) or ClO_4^-) were prepared. Polymeric complexes were found, for the first time, to undergo spin-crossover behaviour. The spin-state interconversion rates were different from those of the corresponding monomeric complexes. On the other hand, [Fe(psalten = *m*) (pvp = *n*)]BPh_4 showed a faster spin-state interconversion rate than the life time of the Mössbauer excited state (1×10^{-7} s). The spin-crossover behaviour of the complexes is described in connection with the polymeric/amorphous structure of the complexes.

Introduction

Much progress has been recently made in the study of spin-crossover phenomena [1]. The transition behaviour of a given complex is influenced by the strengths of the Jahn–Teller coupling between the d-electrons and local distortions [2], and of the intermolecular coupling between the intramolecular distortion and/or a lattice strain [3].

Spin-crossover complexes may be sorted into two groups, one is the ‘fast electronic relaxation type’ in which the spin-state interconversion rate is faster than the ^{57}Fe Mössbauer life time (1×10^{-7} s) and the other is the ‘slow electronic relaxation type’. In this classification the ^{57}Fe time scale is selected for experimental convenience. Recently examples showing fast spin-state interconversion rates have been reported [4]. The rate is dependent on the activation energy of the reorganization of the coordination atmosphere of an iron atom and/or crystal packing and on tunnel effect [5].

Most of the work on spin-crossover phenomena has been focused on crystalline monomeric complexes, although iron compounds with linear poly bases have been synthesized [6]. In the present paper the polymeric spin-crossover iron(III) complexes were successfully prepared in order to elucidate the spin-crossover behaviour of the amorphous complexes and to compare it with that of the corresponding monomeric crystalline complexes. They were characterized using ESR and Mössbauer spectroscopies, and magnetic susceptibilities. Schematic structures of the representative ligands and complexes prepared here are presented below.

Experimental

Preparation of polymeric-4-vinylpyridine and copolymers

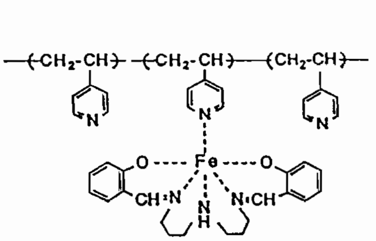
The polymers were synthesized according to the method of Katchalsky *et al.* [7]. The preparation of pvp is as follows. A solution containing 10.1 g of freshly distilled 4-vinylpyridine in 20 ml of ethylalcohol, to which 2,2′-azobisisobutyronitrile (0.045 g) was added, was kept in a closed evacuated tube for 4 days at 70 °C and then the contents of the tube were poured into water. The polymer obtained was purified by repeatedly dissolving in ethyl alcohol and then precipitated with ethyl ether. The polymer was dried *in vacuo* at 50 °C.

Copolymerization of 4-vinylpyridine or 1-vinylimidazole with octylmethacrylate was carried out in a Pyrex tube at 60 °C with 2,2′-azobisisobutyronitrile as indicator

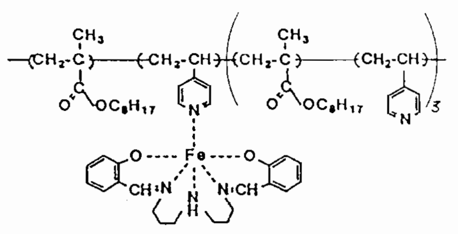
---

*Author to whom correspondence should be addressed.

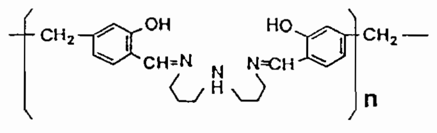
0020-1693/93/$6.00 © 1993 – Elsevier Sequoia. All rights reserved



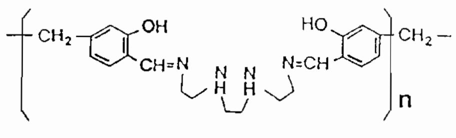
[Fe(salten)(pvp=3)]$^+$



[Fe(salten)(pomp=4)]$^+$



psalten=n



psal$_2$trien=n

[8]. Detailed properties of the polymers prepared by this method are given by Katchalsky *et al.* [7]. The polymeric Schiff bases with a degree of polymerization (*Pn*) above 100 were prepared by this method.

Preparation of [Fe(salten) (pvp=4)]BPh$_4$ (1)

The Schiff base solution was prepared by refluxing a mixture of ethyl alcohol (25 ml) containing 0.77 g of salicylaldehyde and ethyl alcohol (25 ml) containing 0.41 g of dipropylenetriamine for 1 h. It was used without purification. Complex **1** was prepared by adding ethyl alcohol (10 ml) containing 0.10 g of ^{57}Fe doped iron chloride into the above Schiff base solution (an amount of one-fifth in volume was used). To the solution made in this way was added slowly a solution of ethyl alcohol (25 ml) containing 0.26 g of pvp, after which the solution was kept under stirring at room temperature for 5 h. Ethyl alcohol (5 ml) containing 0.43 g of $NaBPh_4$ was very slowly added, the solution was further stirred for 6 h, and the precipitations were filtered with a sintered glass filter, washed with ethyl alcohol and dried *in vacuo*. *Anal.* Found: C, 75.08; H, 6.47; N, 8.91; Fe, 4.63. Calc. for $BC_{72}FeH_{70}N_7O_2$: C, 76.41; H, 6.19; N, 8.67; Fe, 4.94%. 'pvp = 4' in the chemical formula means that the ratio number of vinylpyridine/number of iron in the molecule is four.

[Fe(salten) (pomp=3)]BPh$_4$ (**2**) and [Fe(salten) (pomi=3)]BPh$_4$ (**3**) were prepared by a method similar to that described above using pomp and pomi instead of pvp, respectively. *Anal.* Found for complex **2**: C, 75.02; H, 8.18; N, 4.36; Fe, 2.98. Calc. for $BC_{108.2}FeH_{142.2}N_6O_{9.2}$: C, 74.69; H, 8.18; N, 4.83; Fe, 3.21%. Found for complex **3**: C, 71.77; H, 8.82; N, 4.73; Fe, 1.84. Calc. for $BC_{159.8}FeH_{244.8}N_9O_{18.8}$: C, 72.20; H, 9.22; N, 4.74; Fe, 2.10%.

Preparation of [Fe(psalten=m) (pvp=n)]ClO$_4$ (4) and [Fe(psal$_2$trien=m)]BPh$_4$(pvp=n) (5)

5,5′-Methylene-bis-salicylaldehyde was obtained by treating salicylaldehyde with trioxane. Schiff bases psalten and psal$_2$trien were synthesized using dipropylenetriamine and 5,5′-methylene-bis-salicylaldehyde, and using triethylenetetramine and 5,5′-methylene-bis-salicylaldehyde as described by Goodwin and Bailar [9], respectively. Complex **4** was prepared by the following method. ^{57}Fe doped $Fe(ClO_4)_3 \cdot 9H_2O$(0.041 g) dissolved in *N,N*-dimethylformaldehyde (dmf, 10 ml) was slowly added to a solution of dmf (30 ml) containing 0.10 g of psalten under heating. The mixture solution was stirred for 6 h and then filtered. A solution of dmf (20 ml) containing 0.76 g of pvp was very slowly added into the filtrate and the mixed solution was stirred for 6 h and then filtered. The filtrate was slowly added to a solution (200 ml) of ethyl ether. The rubber-like solids deposited were filtered with a sintered glass filter and dried *in vacuo*.

Complex **5** was obtained in a similar manner by using ^{57}Fe doped $FeCl_3$ (0.015 g) instead of $Fe(ClO_4)_3 \cdot 9H_2O$ and triethylenetetramine instead of dipropylenetriamine, and adding 0.061 g $NaBPh_4$ in dmf (5 ml). The identity of these complexes was confirmed analytically and spectroscopically, although the values of *m* and *n* were not determined because of the complex composition of the compounds. The ratio number of octylmethacrylate/number of 4-vinylpyridine in pomp was 1:2 and the ratio number of octylmethacrylate/number of 1-vinylimidazole in pomi was 2:8 from the elemental analysis results of the polymers.

Physical measurements

The Mössbauer ^{57}Fe spectra and magnetic susceptibilities for the complexes were measured using equipment previously described [10]. The spectra measured were fitted to two doublets with Lorentzian line shapes, except the datum at 4.2 K, using a least-squares method at the Computer Center, Kyushu University. Isomer shifts δ are reported with respect to the centroid of the spectrum of iron foil enriched with ^{57}Fe at 296 K. The ESR measurements were performed with a FES-FEX (Jeol, Ltd.) spectrometer at X-band frequencies.

Results and discussion

Although the elemental analysis of the complexes prepared here was carried out, it is not easy to determine the accurate stoichiometry of the complexes.

Powder X-ray diffraction patterns were measured for the salten complexes, but no reflection patterns were observed and so the complexes are non-crystalline.

The complexes prepared here are from blue to violet in colour at room temperature and the colours turn to green or greenish blue at 78 K in coincidence with the change of the spin-state of the iron(III) atoms.

Magnetic susceptibilities for the complexes

The temperature dependences of the magnetic moments for complexes **1**, **2** and **3** are shown in Fig. 1, and the reciprocal gram magnetic susceptibilities for complexes **4** and **5** are plotted in Fig. 2. The values of the magnetic moments/reciprocal gram magnetic susceptibilities for the complexes are dependent on temperature and it is obvious from the figures that high- and low-spin iron(III) complexes coexist over a wide temperature range.

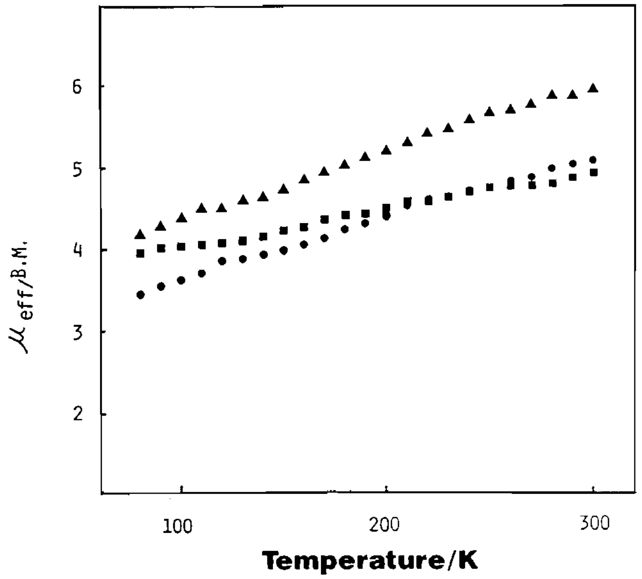


Fig. 1. The temperature dependences of magnetic moments for complexes **1** (●), **2** (■) and **3** (▲).

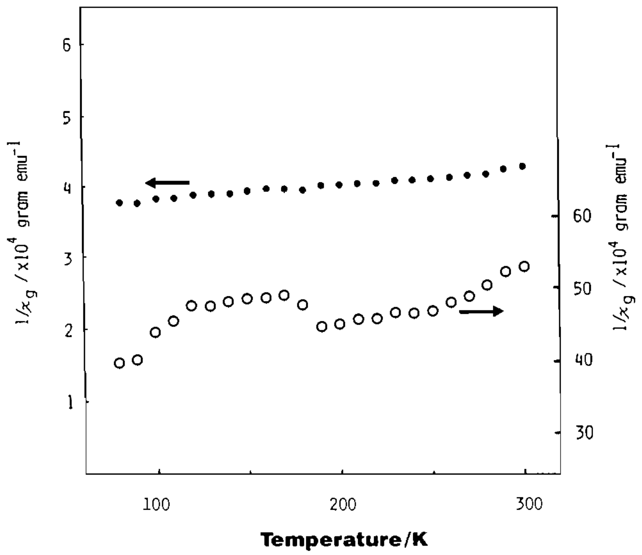


Fig. 2. The temperature dependences of the reciprocal gram magnetic susceptibilities for complexes **4** (●) and **5** (○).

The monomeric salten complexes with 4-vinylpyridine do not undergo spin-crossover behaviour although the corresponding complexes with pyridine derivatives, except 4-vinylpyridine, and the polymeric salten complex undergo spin transition. These results support the fact that polymerization of 4-vinylpyridine makes it more basic [11].

The psal$_2$trien complexes containing no pvp show spin-crossover behaviour dependent on temperature in dmf solution, but the solid of the complexes does not show spin-crossover behaviour. However, if the psal$_2$trien complexes containing a large amount of pvp are precipitated in dmf solution by adding ethyl ether, the solid precipitated shows spin-crossover behaviour. Therefore, the polymeric pvp plays the role of 'solid solvent' in the complexes. The scattered/isolated presence of molecules of the complexes in the pvp solid would be expected to facilitate the reorganization of the coordination sphere of the iron atoms with spin-state transition.

ESR spectra for the complexes

ESR spectra for the complexes were measured and representative examples are shown in Figs. 3, 4 and 5. The relevant g values at 78 K are 1.835, 2.073, 2.604 and 4.210 for complex **1**; 1.827, 2.054, 2.567 and 4.226 for complex **2**; and 1.819, 1.985, 2.654 and 4.238 for complex **3**. The signals of g = about 4 are assigned to high-spin iron ions in distorted octahedral structures and the other three signals are assigned to low-spin iron(III).

Those for complex **4** are observed at 1.833, 2.068, 2.538 and 4.288 at 18 K, which are almost identical with those for [Fe(salten)P]X. These g tensor components for the low-spin isomers were analyzed by the

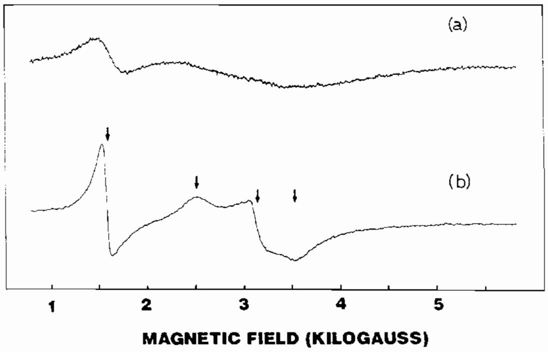


Fig. 3. ESR spectra for complex **1** at (a) 296 and (b) 78 K.

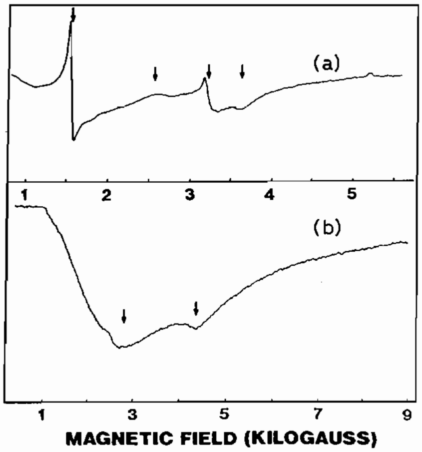


Fig. 4. ESR spectra for complex **4** at (a) 18 K and (b) 296 K.

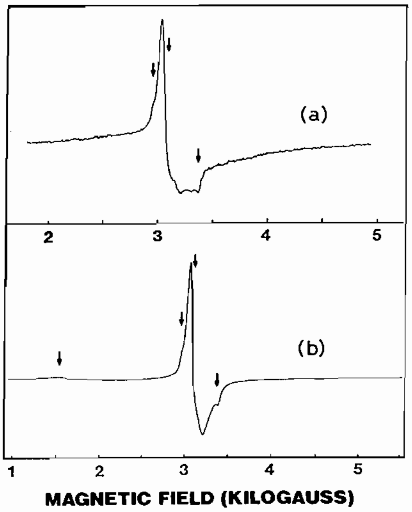


Fig. 5. ESR spectra for complex **5** at (a) 296 K and (b) 18 K.

method of Bohan [12]. The following states for the Kramers doublet were used:

$$|\psi_i^+\rangle = A_i|+1,\ \alpha\rangle + B_i|\zeta,\ \beta\rangle + C_i|-1,\ \alpha\rangle \quad i=1,\ 2,\ 3$$

$$|\psi_i^-\rangle = A_i|-1,\ \beta\rangle - B_i|\zeta,\ \alpha\rangle + C_i|+1,\ \beta\rangle \quad i=1,\ 2,\ 3$$

This analysis indicates that the unpaired electron resides in a d_{zx} orbital ($A=0.8195$, $B=0.0608$, $C=0.5710$; $E_A=7.97\ \lambda$, $E_R=0.29\ \lambda$, $E1=-4.20\ \lambda$, $E2=-1.12\ \lambda$, $E3=5.26\ \lambda$ for complex **4**) as the most reasonable assignment, where λ is the spin–orbit coupling constant, E_A is the axial ligand field distortion parameter and E_R gauges the rhombic distortion.

The g values for complex **5** are 1.965, 2.147 and 2.238 at 296 K, and 1.958, 2.149, 2.236 and 4.376 at 18 K, compared with the values for the monomeric complex $[Fe(sal_2trien)]BPh_4\cdot$ acetone; of 1.944, 2.194, and 2.220 (at 78 K). These values are characteristic of low-spin iron(III) ions in a distorted octahedral field.

The above data exhibit that the low- and high-spin isomers coexist at low temperatures. It should be said that the coordination atmospheres of low-spin iron atoms are similar to one another in the solid, because the signals for the low-spin isomers are rather sharp.

Mössbauer spectra for [Fe(salten)P]BPh₄

The temperature dependences of the Mössbauer spectra for the complexes were measured. Figure 6

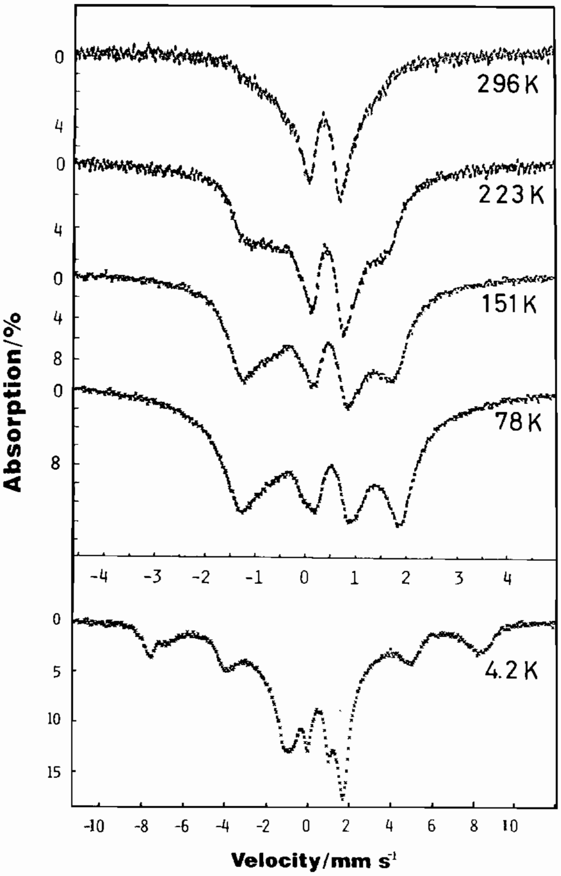


Fig. 6. The temperature dependence of the Mössbauer spectra for complex **1**.

shows the Mössbauer spectra of complex **1** at various temperatures. The relevant Mössbauer parameters are listed in Table 1 with the results for the other complexes. The spectra, except the spectrum at 4.2 K were fitted to two doublets. The spectra consist of an inner doublet due to the high-spin isomers and an outer one due to the low-spin isomers in accordance with the magnetic susceptibility results. The ratio of the absorption area of the low-spin isomers to the total absorption area increases from 40.2% at 296 K to 68.3% at 78 K.

New absorptions with an internal magnetic field of 48.5 Tesla appear in addition to those of the low- and high-spin isomers in the spectrum at 4.2 K. This fact suggests the existence of three different chemical species in the complexes; the first show spin-crossover behaviour, the second are high-spin paramagnetic isomers and the third are high-spin isomers with a magnetic hyperfine structure at 4.2 K. The third isomers may be isolated molecules.

The temperature dependences of the Mössbauer spectra for complexes **2** and **3** are shown in Figs. 7 and 8, respectively. High-spin isomers are also observed at 78 K in accord with the magnetic susceptibility results. From the Mössbauer spectra for complex **3** the spin-state interconversion rates are estimated to be comparable with the Mössbauer time scale (the inner doublet observed is due to high-spin isomers which do not show spin-crossover behaviour). It can be said that copolymerization of methylmethacrylate and 1-vinylimidazole makes the reorganization of the coordination atmosphere of the iron atoms with spin-state transition easy because [Fe(salten)(pvi = 3)]BPh_4 (pvi = polymeric-1-vinylimidazole, the detailed magnetic property of the complex is not described here) is a high-spin complex at temperatures of 78 to 300 K. The monomeric complex [Fe(salten)(2Me-Im)]BPh_4 (2Me-Im = 2-methylimidazole) is a spin-crossover complex with rapid spin-state interconversion rates [11] and the Mössbauer parameters of this monomer ($\delta = 0.284$ mm/s and $\Delta E = 2.716$ mm/s at 78 K) are comparable with those for complex **3**. It can be said that the chemical/geometrical structure around the iron atoms of the polymeric complexes is similar to those of the corresponding monomeric analogs and that the polymerization/amorphousness of the complex effects the second or higher order structure of the polymeric complexes.

Mössbauer spectra for complexes 4 and 5

The temperature dependences of the Mössbauer spectra of complexes **4** and **5** are given in Figs. 9 and 10, respectively, and the Mössbauer parameters are collected in Table 1. The spectra of Fig. 9 can be fitted to two doublets (spin-crossover component and high-spin one) consistent with the magnetic susceptibility results, and the values of the quadrupole splittings

TABLE 1. Mössbauer parameters for complexes **1–5**

Temperature (K)	δ[a] (mm/s)	ΔE[b] (mm/s)	F[c] (%)
Complex **1**			
296	0.416	0.733	59.8
	0.301	2.075	40.2
223	0.462	0.811	45.4
	0.280	2.552	54.6
151	0.507	0.862	36.5
	0.289	2.874	63.5
78	0.520	0.852	31.7
	0.351	2.990	68.3
4.2	0.530	1.010	14.2
	0.521	0.185	28.7[d]
	0.401	2.644	57.1
Complex **2**			
296	0.282	1.120	75.8
	0.244	2.029	24.2
200	0.346	1.148	34.1
	0.230	2.315	65.9
78	0.339	1.019	2.4
	0.441	2.503	97.6
Complex **3**			
296	0.447	1.157	86.6
	0.202	2.669	13.4
252	0.473	1.224	70.1
	0.202	2.620	29.9
200	0.550	1.501	70.8
	0.207	2.548	29.2
150	0.566	1.692	54.3
	0.208	2.618	45.7
78	0.610	1.564	40.8
	0.380	3.052	59.2
4.2	0.682	1.528	21.9
	0.559	0.122	26.0[d]
	0.451	3.001	53.1
Complex **4**			
340	0.341	1.103	59.5
	0.250	1.674	40.5
320	0.326	1.140	55.8
	0.243	2.032	44.2
296	0.340	1.153	50.2
	0.223	2.190	49.8
200	0.343	1.173	50.8
	0.226	2.615	49.2
78	0.331	1.220	39.0
	0.301	2.822	61.0
Complex **5**			
315	0.297	0	72.5
	0.120	2.401	27.5
296	0.307	0	50.2
	0.166	2.492	49.8
250	0.350	0	45.6
	0.147	2.576	54.4
200	0.372	0	24.7
	0.172	2.636	75.3
150	0.375	0	18.0
	0.193	2.639	82.0
78	0.520	0	15.7
	0.211	2.641	84.3

[a] Isomer shift relative to iron metal. [b] Quadrupole splitting. [c] Absorption area ratio to the total absorption area. [d] This absorption line shows a magnetic hyperfine structure.

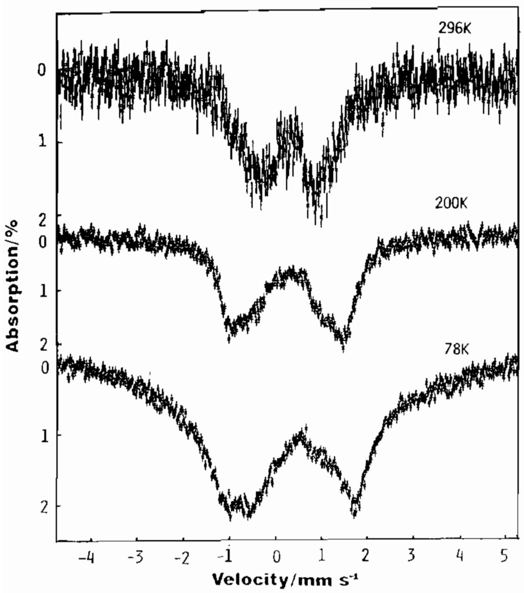


Fig. 7. The temperature dependence of the Mössbauer spectra for complex **2**.

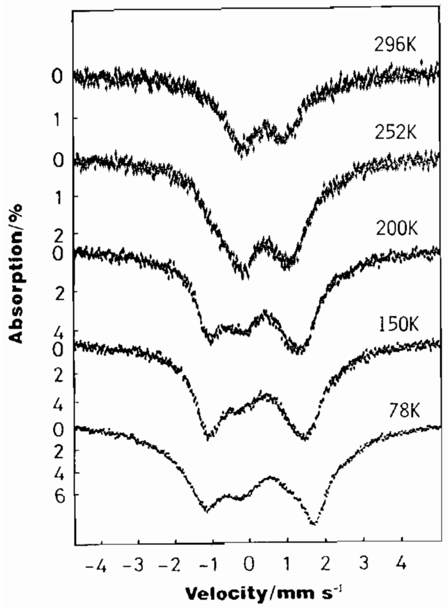


Fig. 8. The temperature dependence of the Mössbauer spectra for complex **3**.

assigned to the isomers showing spin-crossover decrease with an increase in temperature. From the ESR results for complex **4** it is clear that there is not a low excited electronic energy level which leads to change in electric field gradient (efg). Therefore Fig. 9 shows spectral changes characteristic of complexes showing fast spin-state interconversion and the rates of complex **4** are faster than those of complex **1**; the polymerization of the Schiff base brings about faster spin-state interconversion rates. Figure 10 shows slow interconversion rates and the amount of the high-spin isomers observed at 78 K is estimated to be 15.7% from the ratio of the absorption area.

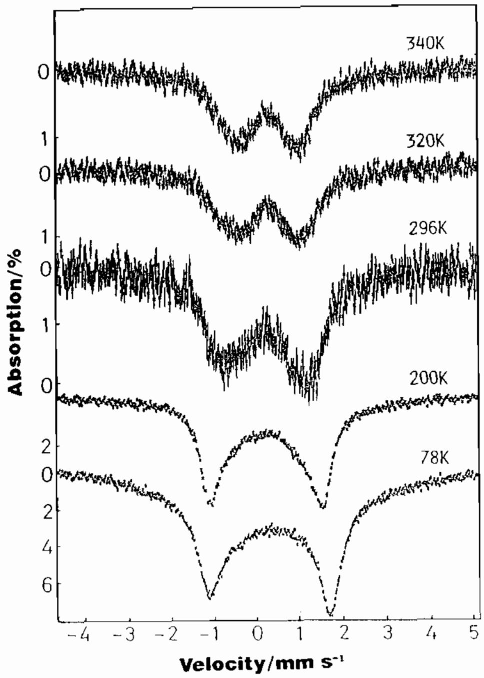


Fig. 9. The temperature dependence of the Mössbauer spectra for complex **4**.

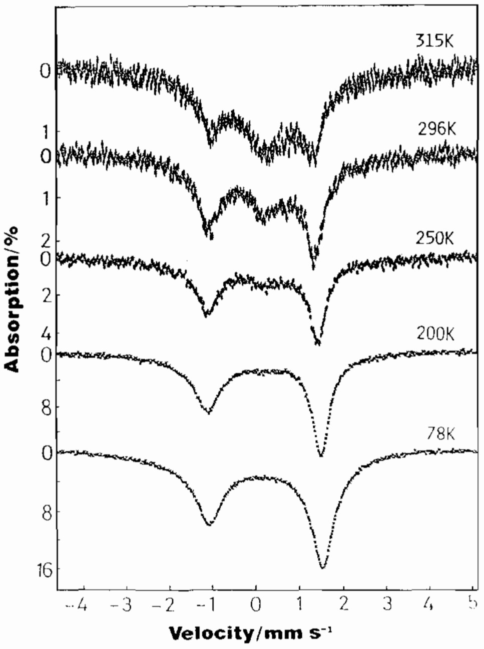


Fig. 10. The temperature dependence of the Mössbauer spectra for complex **5**.

Monomeric [Fe(sal$_2$trien)]BPh$_4$ acetone is prepared in two crystal forms from ethyl alcohol solution; one is a spin-crossover complex (minority isomers) and the other a high-spin complex (majority isomers) [13]. However, spin-crossover complexes contained in the polymeric psal$_2$trien complexes are in the majority. The high-spin isomers are estimated to be the isomers of the spin-crossover complex because the Mössbauer parameters of the high-spin isomers are in accord with those of the monomeric high-spin complexes ($\delta = 0.27$, $\Delta E = 0$ mm/s at 296 K).

The full widths at half maximum of these polymeric complexes, i.e. 0.56–0.72 and 0.95–1.24 mm/s for complex **4** at 78 K are broad in comparison with those of the corresponding monomeric analogs. One of the reasons is due to the long iron–iron atomic distances. The second is that coordination geometries around the iron atoms in limited amounts are different from each other.

Conclusions

The complexes prepared here undergo spin-crossover, and the polymerization/amorphousness of the complexes strongly influences the temperature ranges in which the complexes undergo spin-state transition, and weakly influences the transition rates and the intermolecular interaction rather than the intramolecular interaction in comparison with interactions in monomeric crystalline analogs. Iron atoms are different from one another in the intermolecular atmosphere rather than in the intramolecular coordination atmosphere, and the spin-state transition temperatures vary from one iron atom to another.

References

1 (a) P. Gütlich, *Struct. Bonding (Berlin), 44* (1981) 83; (b) E. König, G. Ritter and S. K. Kulshreshtha, *Chem. Rev., 85* (1985) 219; (c) M. S. Haddad, M. W. Lynch, W. D. Federer and D. N. Hendrickson, *Inorg. Chem., 20* (1981) 123; (d) Y. Maeda and Y. Takashima, *Comments Inorg. Chem., 7* (1988) 41.

2 T. Kambara, *J. Chem. Phys., 70* (1979) 4199.

3 (a) T. Sasaki and T. Kambara, *J. Chem. Phys., 74* (1981) 3472; (b) T. Kambara, *J. Chem. Phys., 74* (1981) 4557.

4 (a) Y. Maeda, N. Tsutsumi and Y. Takashima, *Chem. Phys. Lett., 88* (1982) 248; (b) M. D. Timken, A. M. Abdel-Mawgoud and D. N. Hendrickson, *Inorg. Chem., 25* (1986) 160.

5 A. J. Conti, C.-L. Xie and D. N. Hendrickson, *J. Am. Chem. Soc., 111* (1989) 1171.

6 (a) E. Tsuchida, H. Nishide and M. Takeshita, *Makromol. Chem., 175* (1974) 2293; (b) C. Decoene and P. Teyssie, *J. Polym. Sci., 57* (1962) 121; (c) W. Sawodny and M. Riederer, *Angew. Chem., 89* (1977) 897; (d) E. Tsuchida, K. Shigehara and Y. Kurimura, *J. Polym. Sci., 12* (1974) 2207.

7 A. Katchalsky, K. Rosenheck and B. Altmann, *J. Polym. Sci., 23* (1957) 955.

8 T. Tamikado, *J. Polym. Sci., 43* (1960) 489.

9 H. A. Goodwin and J. C. Bailar, Jr., *J. Am. Chem. Soc., 83,* (1961) 2467.

10 H. Oshio, K. Kitazaki, J. Mishiro, N. Kato, Y. Maeda and Y. Takashima, *J. Chem. Soc., Dalton Trans.,* (1987) 1341.

11 N. Matsumoto, S. Ohta, C. Yoshimura, A. Ohyoshi, S. Kohata, H. Okawa and Y. Maeda, *J. Chem. Soc., Dalton Trans.,* (1985) 2575.

12 T. L. Bohan, *J. Magn. Reson., 26* (1977) 109.

13 Y. Maeda, H. Oshio, Y. Tanigawa, T. Oniki and Y. Takashima, *J. Chem. Soc. Jpn., 64* (1991) 1522.