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Studies of Iron(II) Complexes with Several Schiff Bases: New Examples of $^5T_2$-$^1A_1$ Equilibrium

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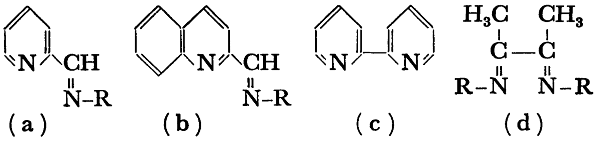
Iron complexes with the Schiff bases of quinolinecarbaldehyde and pyridinecarbaldehyde were prepared. Mössbauer spectra and magnetic susceptibilities of the compounds, $Fe(pipa)_2(NCS)_2$, $Fe(pa)_2(NCS)_2$, $Fe(pot)_2(NCS)_2 \cdot 1/2CHCl_3$, $Fe(ppt)_2(NCS)_2$, $Fe(ppca)_2(NCS)_2$, and $Fe(ppa)_2(NCS)_2$ were studied in the temperature range between 298 and 27 K. It was found that these complexes showed an incomplete $^5T_2$-$^1A_1$ transition in the solid. The compound $Fe(poca)_2(NCS)_2$ also showed a similar phenomenon. The observations of the behavior of the various complexes indicated that the magnetic changeover from spin-paired to spin-free would be closely associated with a modification of the crystal lattice. The $FeL'Cl_2$(L′: the Schiff bases of quinolinecarbaldehyde) were found to have distorted tetrahedral structures.

The spectral study of a substantial series of complexes derived from the Schiff bases of 2-pyridinecarbaldehyde has already been completed.[1] The iron(II) complexes of *N*-(2-pyridylmethylene)methylamine exhibit quite similar magnetic and spectroscopic behavior to that of the iron(II) complexes of 2,2′-bipyridine and 1,10-phenanthroline. A series of iron(II) complexes with the Schiff bases of quinolinecarbaldehyde and pyridinecarbaldehyde were prepared. The spectroscopic and magnetic properties of some compounds possessing anomalous magnetic properties are reported in this work. From a structural point of view, the iron complexes with the Schiff bases of quinolinecarbaldehyde and pyridinecarbaldehyde are well correlated with those of 2,2′-bipyridine and aliphatic α,α′-diimine, *i.e.*, they all contain –N=C–C=N group which directly participates in the co-ordination. As may readily be seen in the figure, however, the Schiff bases of pyridinecarbaldehyde(a) and quinolinecarbaldehyde(b) are in an intermediate state between 2,2′-bipyridine(c), and α,α′-diimine(d) compounds with respect to the conjugated double bond.



It has been observed that certain iron(II) complexes of 2,2′-bipyridine,[2] 1,10-phenanthroline,[3] and 2-(aminomethyl)pyridine[4] have magnetic moments which are dependent on temperature. It was suggested that the intermediate magnetic moment might be due to a thermal equilibrium between the high- and low-spin states. Recently iron(II) compounds which exhibit an incomplete $^5T_2$-$^1A_1$ transition have been reported.[5]

Experimental

Materials. Quinoline derivatives were prepared from 2-quinolinecarbaldehyde and aromatic or aliphatic amines. The preparation of the 2-quinolinecarbaldehyde was accomplished by reduction of ω,ω-dibromoquinaldine with silver nitrate.[6] 2-Pyridinecarbaldehyde was purchased from the Ishizu Pharmaceutical Co., Ltd. The ligand abbreviations used in this work are, qa for *N*-(2-quinolylmethylene)aniline, qipa for *N*-(2-quinolylmethylene)isopropylamine, qot for *N*-(2-quinolylmethylene)-*o*-toluidine, qpt for *N*-(2-quinolylmethylene)-*p*-toluidine, qea for *N*-(2-quinolylmethylene)ethylamine, qba for *N*-(2-quinolylmethylene)benzylamine, pa for *N*-(2-pyridylmethylene)aniline, pipa for *N*-(2-pyridylmethylene)isopropylamine, pot for *N*-(2-pyridylmethylene)-*o*-toluidine, ppt for *N*-(2-pyridylmethylene)-*p*-toluidine, ppna for *N*-(2-pyridylmethylene)-*p*-nitroaniline, ppca for *N*-(2-pyridylmethylene)-*p*-chloroaniline, poca for *N*-(2-pyridylmethylene)-*o*-chloroaniline, ppa for *N*-(2-pyridylmethylene)-*p*-anisidine, pba for *N*-(2-pyridylmethylene)benzylamine and ph for 2-pyridinecarbaldehyde hydrazone.

Preparations of the Complexes. The complexes were prepared by mixing iron(II) salts and the Schiff bases in an ethanolic solution.

The crystals were collected and recrystallized from water, acetone or chloroform. To avoid any possible oxidation, the procedures were carried out in a nitrogen atmosphere, using air-free ethanol. The complexes are generally stable to oxidation in the solid state. The complexes, however, were stored in a nitrogen atmosphere. The complexes prepared are listed in Table 1 together with analytical and magnetic data. Microanalyses were carried out at the Elemental Analysis Center of Kyushu University.

Measurements. Mössbauer effect measurements were made with a spectrometer described elsewhere.[7] Cobalt-57 diffused into palladium foil was used as the source. The isomer shifts, δ_N, were measured relative to the center of the spectrum of sodium nitroprusside which was used as velocity calibration. The absorbers used are very thin of approximately 0.067 mg of ^{57}Fe per cm^2 so that the saturation effect becomes negligible. The transmitted counts were stored at the rate of 60000—600000 counts per channel over a period of 18—50 h to minimize the statistical error. Magnetic susceptibilities between 77 and 295 K were measured on the polycrystalline samples by the Faraday method, while magnetic susceptibilities at 295 K were measured by the Gouy method. $HgCo(NCS)_4$ was used as the calibration substance.

Diamagnetic corrections were made for the ligands and anions. The effective magnetic moment, μ_{eff}, was obtained from the relation $\mu_{eff}=2.83\sqrt{\chi_m T}$, where χ_m is the molar susceptibility after applying diamagnetic corrections.

Reflectance and infrared spectra were obtained with apparatus described elsewhere.[8]

The conductivities of the complexes in one of solutions of acetone, chloroform and water, were measured using a Yanagimoto bridge and a cell which had been previously calibrated with aqueous KCl solutions.

Table 1. ANALYTICAL AND MAGNETIC DATA

Complexes	Found (%) C	Found (%) H	Found (%) N	Calcd (%) C	Calcd (%) H	Calcd (%) N	μ_{eff}(BM.) at 295K
$Fe(qa)Cl_2$	53.03	3.32	7.68	53.48	3.34	7.80	5.06
$Fe(qipa)Cl_2$	48.00	4.30	8.52	48.00	4.31	8.62	5.12
$Fe(qot)Cl_2$	54.70	3.89	7.44	54.69	3.75	7.51	5.11
$Fe(qpt)Cl_2$	54.87	3.71	7.39	54.69	3.75	7.51	5.17
$Fe(qea)_2(NCS)_2$	57.21	4.41	15.23	57.79	4.45	15.56	5.48
$Fe(qba)_2(NCS)_2$	64.92	12.56	4.30	65.07	12.65	4.22	5.52
$Fe(qea)_2Cl_2 \cdot 1/2H_2O$	56.75	5.05	10.60	57.14	4.96	11.11	5.39
$Fe(qba)_2Cl_2 \cdot 1/2H_2O$	64.38	4.71	8.61	64.97	4.62	8.92	5.30
$Fe(pa)_2Cl_2$	58.42	4.29	11.24	58.66	4.07	11.41	5.13
$Fe(pipa)_2(NCS)_2$	51.37	5.28	18.03	51.29	5.13	17.95	4.33
$Fe(pa)_2(NCS)_2$	58.27	3.81	15.81	58.22	3.73	15.67	5.30
$Fe(pot)_2(NCS)_2 \cdot 1/2CHCl_3$	55.08	4.12	13.13	54.84	3.93	13.47	5.32
$Fe(ppt)_2(NCS)_2$	58.76	4.20	14.77	59.59	4.26	14.90	5.15
$Fe(ppna)_2(NCS)_2$	50.00	3.22	17.33	49.85	2.88	17.89	5.41
$Fe(ppca)_2(NCS)_2$	51.44	3.17	13.62	51.66	2.98	13.91	5.45
$Fe(poca)_2(NCS)_2$	51.24	3.48	14.03	51.66	2.98	13.91	5.48
$Fe(ppa)_2(NCS)_2$	56.05	3.97	13.92	56.19	4.01	14.05	5.17
$Fe(pba)_3(NCS)_2 \cdot H_2O$	63.27	5.52	14.50	63.24	4.88	14.40	1.13
$Fe(ph)_3(NCS)_2$	44.56	4.01	28.73	44.86	3.93	28.79	0.85

Table 2. CONDUCTIVITY DATA OF SOME IRON COMPLEXES (10^{-3}M)

Complexes	Λ_m (mho cm^{-2} mol^{-1})	Solvent[1]
$Fe(pa)_2Cl_2$	22.0	A
$Fe(pa)_2(NCS)_2$	4.3	A
$Fe(pot)_2(NCS)_2 \cdot 1/2CHCl_3$	0.1	A
$Fe(ppt)_2(NCS)_2$	0.1	A
$Fe(pba)_3(NCS)_2 \cdot H_2O$	149.0	W
$Fe(ph)_3(NCS)_2$	150.3	W
$Fe(poca)_2(NCS)_2$	0	C
$Fe(ppca)_2(NCS)_2$	0	C
C $Fe(ppa)_2(NCS)_2$	0	C

The measurements were performed at 25 °C. Abbreviations: A: acetone, C: chloroform, W: water.

Results and Discussion

All the complexes prepared are listed in Table 1. The results obtained by elemental analysis agreed well with the calculated values. The effective magnetic moments at 295 K are also listed in the Table 1.

Conductivities. The molar conductivities of these complexes described in Table 2 exhibit a pattern consistent with their proposed structures. The iron complexes $Fe(pa)_2Cl_2$, $Fe(pa)_2(NCS)_2$, $Fe(pot)_2(NCS)_2 \cdot 1/2CHCl_3$, $Fe(ppt)_2(NCS)_2$, $Fe(poca)_2(NCS)_2$, $Fe(ppca)_2(NCS)_2$, and $Fe(ppa)_2(NCS)_2$ were non-electrolytic in acetone or chloroform. The molar conductivities of a water solution of $Fe(pba)_3(NCS)_2 \cdot H_2O$ and $Fe(ph)_3(NCS)_2$ show that the compounds behave as uni-bivalent electrolytes. The conductivities of some of these compounds are not listed in Table 2, because they could not be determined owing to their low solubility in organic solvents.

Mössbauer Spectra. For an $Fe^{2+}(d^6)$ system, a separate Mössbauer transition could be observed for the high and low-spin states. The time of change from one spin state to the other must therefore be longer than 1×10^{-7} s, the lifetime of the ^{57}Fe excited state. The ^{57}Fe Mössbauer data obtained are given in Tables 3 and 4. The Mössbauer spectra of compounds $Fe(pipa)_2(NCS)_2$, $Fe(pa)_2(NCS)_2$, $Fe(pot)_2(NCS)_2 \cdot 1/2CHCl_3$, $Fe(ppt)_2(NCS)_2$, $Fe(ppa)_2(NCS)_2$, and $Fe(ppca)_2(NCS)_2$ at a variety of temperatures are shown in Figs. 1—6.

The values of the isomer shift and quadrupole splitting of $Fe(pa)_2(NCS)_2$ at 298 K would appear to fall in the region of those characteristic of a high-spin six-coordinated iron(II) compound. The spectrum changes to that of a low-spin iron(II) compound at 27 K, partly leaving the high-spin doublet. This result coincides well with the magnetic susceptibility data which are at intermediate values between those of high-spin and low-spin iron(II) compounds.

On the other hand, the spectrum of $Fe(pipa)_2(NCS)_2$ measured at 298 K consists of superimposed lines that are assigned to high-spin and low-spin iron(II) compounds, respectively. The spectrum changes to the spectrum characteristic of a low-spin iron(II) compound at 196 K, *i.e.*, a small isomer shift and a small quadrupole splitting are observed. The Mössbauer spectra of $Fe(pa)_2Cl_2$, $Fe(pba)_3(NCS)_2 \cdot H_2O$, and $Fe(ph)_3(NCS)_2$, which contain similar ligands, were measured for a comparison of the Mössbauer parameter. The spectrum of $Fe(ppna)_2(NCS)_2$ was also measured at 83 K and iron was found to be in the high-spin state.

In view of the strong electron acceptability of the nitro group, one would expect that the nitrogen atom of imine accepts appreciable electrons providing a strong bond with the iron atom.[9] This expectation, however, was found to be unreasonable as can be seen from the data given in Table 3, *i.e.*, $Fe(ppna)_2(NCS)_2$ is in a high-spin state at 83 K. The differences in the field strengths were not observed for pa, and ppt. The fraction ΔS_L in Table 4 shows the ratio of the absorption

TABLE 3. INFRARED FREQUENCIES AND REFLECTANCE SPECTRAL AND MÖSSBAUER SPECTRAL DATA

Complexes	Vibrational data (cm^{-1})	Reflectance data (cm^{-1})	Mössbauer data (mm/s)			
			at 298 K		at 83 K	
			δ_N	ΔE	δ_N	ΔE
Fe(qipa)Cl$_2$	355^{b,s} 320^{b,m}	25600^m 18500^m 17100^s	1.11	2.78	1.21	2.86
Fe(qa)Cl$_2$	355^{b,s} 325^{b,m}	23100^{w,sh} 17300^s 16500^s	1.13	2.82	1.13	2.80
Fe(qot)Cl$_2$	355^{b,s} 319^{b,m}	25600^{sh} 23500^{sh} 18100^w 16700^m	1.08	2.59	1.13	2.67
Fe(qpt)Cl$_2$	358^{b,s} 353^{b,m} 327^{b,m}	24600^{sh} 23300^{sh} 18200^w 16800^m 15900^{sh}	1.04	2.68	1.16	2.82
Fe(qea)$_2$(NCS)$_2$	2045^c 2060^c	15400^{s,br} 8700^{sh}	1.28	1.86	1.43	2.70
Fe(qba)$_2$(NCS)$_2$	2045^c 2058^c	14900^{s,br}	1.26	1.62	1.43	2.45
Fe(qea)$_2$Cl$_2$·1/2H$_2$O		15300^{s,br}	1.29	2.27	1.42	2.78
Fe(qba)$_2$Cl$_2$·1/2H$_2$O		15300^{s,br}	1.29	1.69	1.40	2.46
Fe(pa)$_2$Cl$_2$	257^b 233^b	26000^m 15200^{s,br}	1.20	2.96	1.33	3.32
Fe(pba)$_3$(NCS)$_2$·H$_2$O	2042^c 2060^c	25400^m 19600^{sh} 17500^s	0.52	0.33	(d)	
Fe(ph)$_3$(NCS)$_2$	2040^c 2060^c	27400^m 22200^{sh} 19200^s	0.55	0.33	(d)	
Fe(pipa)$_2$(NCS)$_2$^{a}	2050^c 2057^c 2100^c	25000^m 19200^{sh} 16300^{s,br}				
Fe(pa)$_2$(NCS)$_2$^{a}	2046^c 2070^c 2100^{c,sh}	24400^{sh} 17500^{sh} 15700^{s,br}				
Fe(pot)$_2$(NCS)$_2$·1/2CHCl$_3$^{a}	2030^c 2060^c 2100^{c,sh}	22000^m 16800^{sh} 15000^{s,br}				
Fe(ppt)$_2$(NCS)$_2$^{a}	2038^c 2055^c	20400^w 16400^{sh} 14600^{s,br}				
Fe(ppna)$_2$(NCS)$_2$	2030^c 2055^c	26000^m 15400^{s,br}	(e)		1.32	3.05
Fe(ppca)$_2$(NCS)$_2$^{a}	2030^c 2045^c	26000^s 15600^{s,br} 9520^s				
Fe(poca)$_2$(NCS)$_2$^{a}	2048^c	29000^s 18000^{sh} 16300^{s,br} 9100^s				
Fe(ppa)$_2$(NCS)$_2$^{a}	2050^c	24000^m 17000^{sh} 15200^{s,bs}				

Abbreviations: (a) Mössbauer parameters for these compounds are summarized in Table 4. (b) Vibration of Fe–Cl. (c) Vibration of NCS. (d) These parameters were not measured. (e) These parameters were not observable. (s) strong, (m) middle, (w) weak, (sh) shoulder, (br) broad.

TABLE 4. MÖSSBAUER PARAMETERS FOR IRON COMPLEXES HAVING SPIN EQUILIBRIUM

Complexes	High-spin state (mm/s)				Low-spin state (mm/s)				ΔS_L
	at 298 K		at 83 K		at 298 K		at 83 K		
	δ_N	ΔE	δ_N	ΔE	δ_N	ΔE	δ_N	ΔE	
Fe(pipa)$_2$(NCS)$_2$	1.22	1.85	a		0.58	0.54	0.63	0.46	1.00
Fe(ppa)$_2$(NCS)$_2$	1.29	2.51	1.27	3.09	a		0.66	0.63	0.74
Fe(ppt)$_2$(NCS)$_2$	1.26	2.65	1.29	3.06	a		0.67	0.68	0.34
Fe(pa)$_2$(NCS)$_2$	1.22	2.47	1.34	3.09	a		0.66	0.70	0.35
Fe(ppca)$_2$(NCS)$_2$	1.24	2.41	1.30	3.09	a		0.67	0.72	0.33
Fe(pot)$_2$(NCS)$_2$·1/2CHCl$_3$	1.28	2.50	1.30	2.93	a		0.62	0.64	0.35
Fe(poca)$_2$(NCS)$_2$	1.25	2.22	1.33	2.88	a		0.59	0.51	0.15

Abbreviation: (a) These absorptions could not be observed.

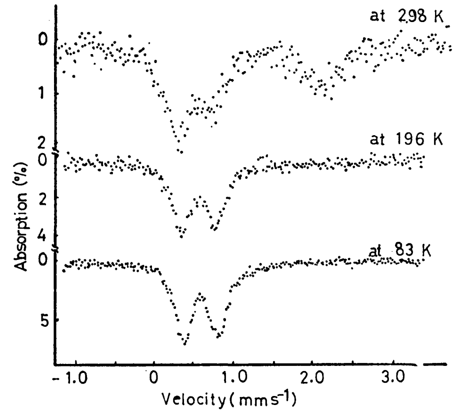


Fig. 1. Mössbauer spectra of Fe(pipa)$_2$(NCS)$_2$ at a variety of temperatures.

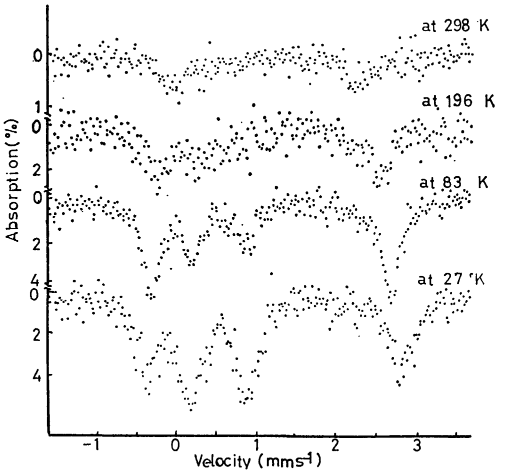


Fig. 2. Mössbauer spectra of Fe(pa)$_2$(NCS)$_2$ at a variety of temperatures.

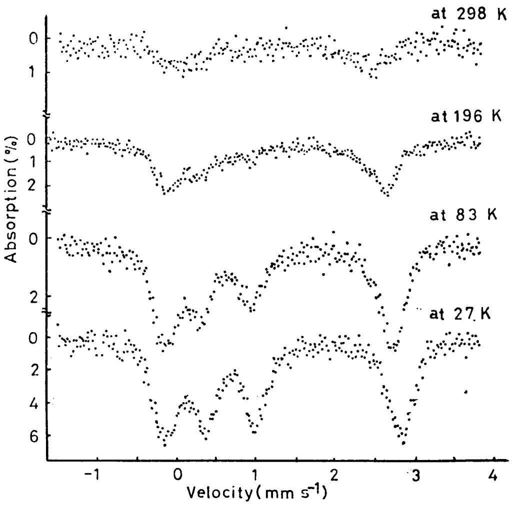


Fig. 3. Mössbauer spectra of $Fe(pot)_2(NCS)_2 \cdot 1/2CHCl_3$ a a variety of temperatures.

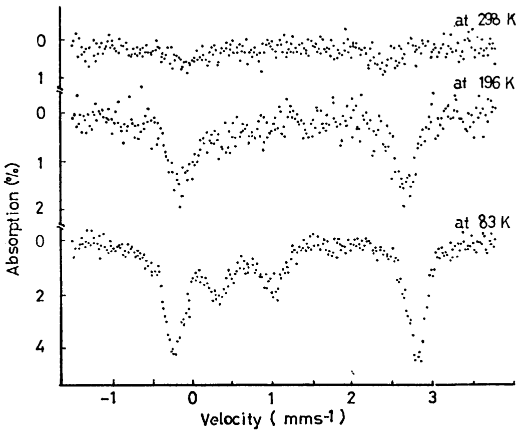


Fig. 4. Mössbauer spectra of $Fe(ppt)_2(NCS)_2$ at a variety of temperatures.

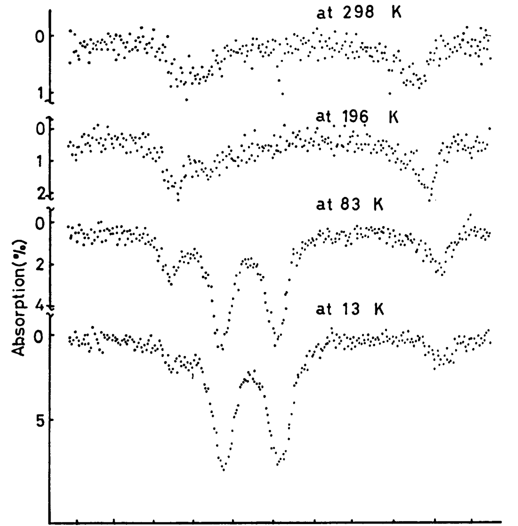


Fig. 5. Mössbauer spectra of $Fe(ppa)_2(NCS)_2$ at a variety of temperatures.

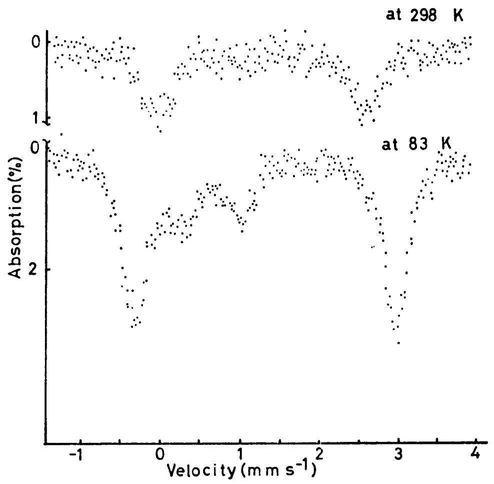


Fig. 6. Mössbauer spectra of $Fe(ppca)_2(NCS)_2$ at a variety of temperatures.

area of iron of the low-spin state to the total absorption area of the Mössbauer spectrum. Based on the general inductive effects of the substituent in the 4-position, it is anticipated that the greater the electronic density of the nitrogen, the greater the ligand-field splitting and the higher the value of Dq. An incomplete transition to the $^1A_1$ state results in a paramagnetic isomer or the existence of a $^5T_2$ excited state having a small energy separation from the $^1A_1$ state. The paramagnetic isomer has still not been observed up to the present time.

The isomer shift of $FeLCl_2$ is smaller than that of FeL_2Cl_2 (L: Schiff bases of quinolinecarbaldehyde or pyridinecarbaldehyde). This fact is interpreted in terms of a tetrahedral structure which is in accordance with the infrared spectral data. The isomer shift of the complexes having a tetrahedral structure is small, in general, because of the smaller s-character or the shielding of the core s-electrons by a larger d-electron contribution.[10)]

The spectra of $Fe(qea)_2(NCS)_2$, $Fe(qba)_2(NCS)_2$, $Fe(qea)_2Cl_2 \cdot 1/2H_2O$, and $Fe(qba)_2Cl_2 \cdot 1/2H_2O$ show a pair of lines at 83 K, which is obviously typical for high-spin iron(II) compounds, although the Schiff bases of quinolinecarbaldehyde are more π-electron acceptable and appear to have a stronger field. This ligand field which is weaker than that of the Schiff bases of pyridinecarbaldehyde might be explained by assuming steric interactions, although the quinoline is a better acceptor of π-electrons than the pyridine. A weaker bond has been observed in the cobalt complexes of quinoline *N*-oxide derivatives.[11)]

The spectra of the compounds, $Fe(ph)_3(NCS)_2$ and $Fe(pba)_3(NCS)_2 \cdot H_2O$, show the small doublet usually observed for low-spin iron(II) compounds.

Magnetic Properties. The temperature dependences of the magnetic moments, in the range of 77—295 K for the complexes $Fe(pipa)_2(NCS)_2$, $Fe(pa)_2(NCS)_2$, and $Fe(ppa)_2(NCS)_2$ are shown in Fig. 7. The magnetic behaviors of the compounds $Fe(pot)_2(NCS)_2 \cdot 1/2CHCl_3$, $Fe(ppt)_2(NCS)_2$, and $Fe(ppca)_2(NCS)_2$ are similar to that of $Fe(pa)_2(NCS)_2$. At low temperatures, the magnetic moment of $Fe(pipa)_2(NCS)_2$ has values

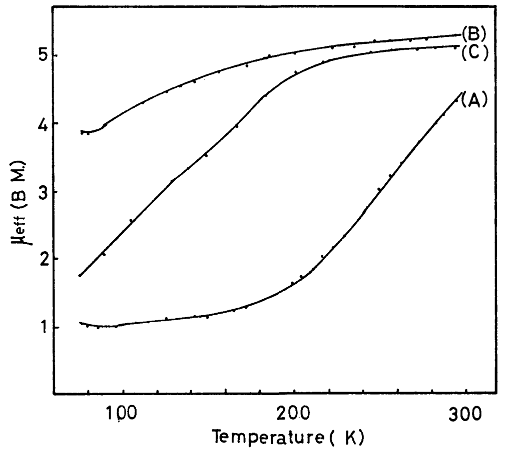


Fig. 7. Variation of the magnetic moment μ_{eff} with temperature for (A) Fe(pipa)$_2$(NCS)$_2$, (B) Fe(pa)$_2$(NCS)$_2$, and (C) Fe(ppa)$_2$(NCS)$_2$.

appropriate to the temperature-insensitive paramagnetism usually found for low-spin iron(II) compounds. It is concluded, therefore, that at 83 K the ground state is in the $^1A_1$ state and that this is the state populated almost exclusively. An interpretation of the magnetic data in terms of an antiferromagnetic-type exchange interaction between neighboring iron atoms is unrealistic since no reasonable fit of the curves for χ_A could be obtained for any value of the exchange coefficient J and since the Mössbauer spectra show that the population of one of the two sites increases with a decrease in temperature. On the other hand, the Mössbauer spectra of the compounds Fe(pa)$_2$(NCS)$_2$, Fe(pot)$_2$(NCS)$_2$·1/2CHCl$_3$, and Fe(ppa)$_2$(NCS)$_2$ show that both high and low-spin states are populated at 27 K and that the transition is incomplete at 27 K (13 K for the last complex). To account for the magnetism of the cross-over compounds theoretically by applying the van Vleck approach[12] is not a good method for this system since such an attempt for systems having spin-paired and spin-free equilibria has failed.[13] For the $^1A_1$-$^5T_2$ equilibrium, the equilibrium constant K_{eq} is given by $K_{eq}=(\mu_O^2-\mu_L^2)/(\mu_H^2-\mu_O^2)$, where μ_H and μ_L are the magnetic moments of the high-spin and low-spin isomers, respectively. Plots of ln K_{eq} *vs.* $1/T$ for Fe(pipa)$_2$(NCS)$_2$ and Fe(pa)$_2$(NCS)$_2$ are given in Fig. 8. This calculation for Fe(pa)$_2$(NCS)$_2$ is based on the assumption that the magnetism of the high-spin state follows a normal Curie-Weiss law, $\chi_m^{corr}=3.7\times10^{-6}/(T+20)$, only over the temperature range from 250 to 300 K. Although using the limited range of temperatures available may introduce considerable uncertainties in the Weiss and Curie constants, the above equation was applied to the lower temperature and μ_H was calculated from this equation. μ_L was taken as 0.8 BM to take into account the temperature-insensitive paramagnetism. For Fe(pipa)$_2$(NCS)$_2$, the same equation was applied.

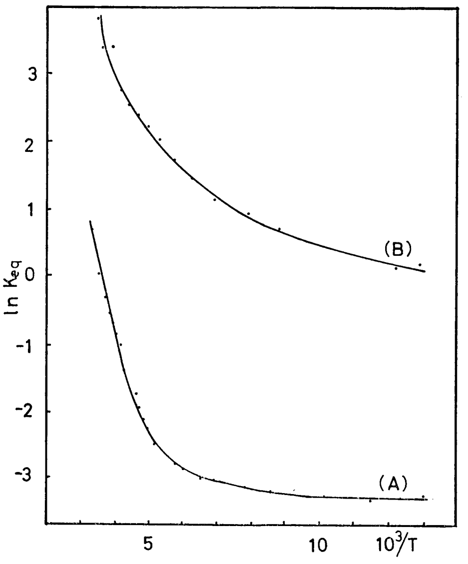


Fig. 8. Curves of ln K_{eq} against $1/T$ for (A) Fe(pipa)$_2$(NCS)$_2$ and (B) Fe(pa)$_2$(NCS)$_2$.

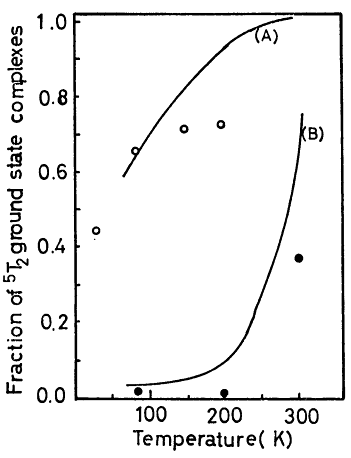


Fig. 9. Plots of the ratio of $^5T_2$ ground state complexes derived from magnetism of Fe(pa)$_2$(NCS)$_2$(A) and Fe(pipa)$_2$(NCS)$_2$(B) with temperature, and the ratio of the spectral area of the iron of high-spin state to the total area of the Mössbauer spectra of A(shown by white circle) and B(shown by black circle) at a variety of temperatures.

The fractions of the $^5T_2$ ground state complexes, n_H, derived from the magnetism of Fe(pa)$_2$(NCS)$_2$ and Fe(pipa)$_2$(NCS)$_2$, are plotted *vs.* T in Fig. 9. The ratio of the absorption area of the high-spin state to the total absorption area, ΔS_H, is also shown for various temperatures in Fig. 9. The Mössbauer spectra of Fe(pa)$_2$(NCS)$_2$ was also measured at 148 K using the melting point of propanol. For Fe(pa)$_2$(NCS)$_2$, $n_L=0.37$ was derived from the magnetic data at 83 K. On the other hand, $\Delta S_L=0.35$ was calculated from the Mössbauer absorption area under the assumption that the Debye-Waller factors, f_H and f_L, were equal. For Fe(ppt)$_2$(NCS)$_2$, $n_L=0.37$ and $\Delta S_L=0.34$ are calculated from the magnetic data and the Mössbauer data, respectively. It is assumed that the Debye-Waller factors, f_H and f_L, are almost equal at 83 K. Fig. 9, however, shows that at temperatures higher than 80 K, ΔS_H is less than n_H. This fact can be accounted for by the differences in the Debye-Waller factors, f_H and f_L, at higher temperatures, that is, f_H is less than f_L. The above differences would result from modifications of the crystal lattice or changes in the bond length between the central metal atom and coordinated atoms.

In the case of *N*-(2-pyridylmethylene)aniline derivatives, the fraction changed to the $^1A_1$ state at 83 K decreases in the order: ppa$>$pa$\approx$ppt$\approx$ppca$>$ppna. This would also be expressed by the order, $-OCH_3>-H\approx-CH_3\approx-Cl>-NO_2$, with respect to the substitutional group. The electron acceptor strength would be expected to increase in the order, $-OCH_3<-CH_3<-H<-Cl<-NO_2$, on the basis of the sigma constant of the Hammett rule. This would seem to explain the fact that the higher electron acceptability of the functional group of the C-4 position brings about decreasing coordinating ability of the N atom in aniline.

The ΔH derived for the magnetic changes of $Fe(pipa)_2(NCS)_2$ remains constant at 3.94 kcal/mol (1380 cm^{-1}) over the temperature range of 224—273 K and is constant at 0.13 kcal/mol (45.5 cm^{-1}) between 87 and 151 K. Between 151 and 224 K ΔH changes continuously. The marked variations of ΔH of the compounds suggest a temperature dependence of the heat capacity of the compounds. Accordingly, it is conceivable that slight modifications of the crystal lattice occur in these compounds.

Electronic Spectra. The reflectance spectra of the iron complexes between 28000 and 4000 cm^{-1} were measured at 298 K. The positions of the absorption maxima are listed in Table 3. The spectra of octahedral iron(II) complexes usually show only comparatively weak bands due to the d-d transitions.[14] The $^5T_{2g}$-$^5E_{2g}$ transition band due to the high-spin form of the complexes which occurs at about 9000—12000 cm^{-1} was not observed, because of very strong charge-transfer bands. The d-d transitions for $Fe(qipa)Cl_2$ and the other substances were also not observed for the same reason, although tetrahedral iron(II) complexes are known to show usually strong band at about 5000 cm^{-1}.

Infrared Spectra. The infrared spectra of iron complexes were studied in the range between 4000 and 200 cm^{-1} at 298 K. Two strong Fe–Cl bands are observed for $Fe(qa)Cl_2$, $Fe(qipa)Cl_2$, $Fe(qot)Cl_2$ and $Fe(qpt)Cl_2$ in accordance with the IR data of $Fe(quinoline)_2Cl_2$[15] which has a tetrahedral structure. It might be assumed from this result that these complexes having $FeLCl_2$-type compositions possess a tetrahedral structure.

For N-bonded thiocyanate, the following absorption ranges are proposed:[16] ν_1 2040—2080, ν_2 465—480, and ν_3 780—860 cm^{-1}. Inspection of Table 3 indicates that in the $^5T_{2g}$ state all the thiocyanates are N-bonded. For $Fe(pipa)_2(NCS)_2$, there is another band at 2100 cm^{-1} at room temperature, which aries from the C–N stretching mode bonded to the iron atom of the $^1A_1$ state,[3] because both the high- and low-spin states are observed in $Fe(pipa)_2(NCS)_2$ at 298 K, as obtained from the Mössbauer spectra and magnetic propoerties. The splitting of the C–N stretching mode is revealed for the $^5T_2$ ground state of some of the complexes by a slight indentation of the main peak. This splitting could be considered to be a *cis*-configuration of the compound.[3] The compounds, $Fe(ppa)_2(NCS)_2$ and $Fe(poca)_2(NCS)_2$, show a sharp absorption for C–N stretching at about 2050 cm^{-1}. The compound, $Fe(pipa)_2(NCS)_2$, shows a very small splitting for C–N stretching at 2050 and 2057 cm^{-1}. This may support for the interpretation of a *trans*-configuration for the compound.

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