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High-Spin($^5T_2$) $\rightleftharpoons$ Low-Spin($^1A_1$) Transition in Mixed Ligand Complex [Fe(2,2′-bipyridine)(1,10-phenanthroline)(NCS)$_2$]

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A new type of the mixed ligand complex [Fe(bpy)(phen)(NCS)$_2$] (bpy=2,2′-bipyridine and phen=1,10-phenanthroline) has been prepared by two different methods. The influence of the mixed ligand coordination of bpy and phen to a central iron(II) ion is studied by measurements of the temperature variation of magnetic moments and Mössbauer parameters. It has been demonstrated that the mixed coordination tends to make the $^5T_2$(high-spin) $\rightleftharpoons$ $^1A_1$(low-spin) transition more gradual. The spin-crossover transition temperature depends on the electronic property as well as the structure of the ligand coordinated to the central iron(II) ion.

A wide variety of bidentate ligands has been studied in an attempt to prepare iron(II) complexes which exhibit the spin-crossover transition $^5T_2$(high-spin) $\rightleftharpoons$ $^1A_1$(low-spin). Almost all spin-crossover iron(II) complexes contain 1,10-phenanthroline (phen), 2,2′-bipyridine (bpy) or their derivatives as bidentate ligands because the ligand field strength of these diamines is intermediate and can afford both high-spin and low-spin states. A few iron(II) complexes of biimidazole and pyridine derivatives are also known to give rise to the spin-crossover transition.[1)] A number of topics concerning the spin-crossover transition in iron(II) complexes has already been fully reviewed in recent articles.[2)] These articles pointed out that the spin-crossover behavior observed for the electronic configuration 3d^6 is affected by some factors such as ligand substitution,[3)] metal dilution,[4)] nature of crystal solvent and anion,[5)] and isotopic substitution.[6)] In spite of much attention to spin-crossover phenomena there have been relatively few reports on the spin-crossover transition of iron(II) complexes with mixed ligands. Exceptionally Spacu et al.[7)] reported the spin-crossover transition of the mixed ligand complex [Fe(py)$_2$(phen)(NCS)$_2$], which stimulated our interest in the preparation of a new mixed-ligand complex for studying the influence of the mixed coordination on spin-crossover behavior.

In the present work we have prepared a new type of the mixed ligand iron(II) complex [Fe(bpy)(phen)(NCS)$_2$] by two different methods. The first method is based on the addition of a methanol solution of iron(II) thiocyanate to a mixed solution of bpy and phen in methanol. The second one is based on stepwise replacing two pyridine ligands of the starting material [Fe(py)$_4$(NCS)$_2$] with a phen, followed by further replacement of the residual two pyridine ligands by a bpy. These two synthetic methods are likely to be very useful in preparing a variety of novel mixed-ligand iron(II) complexes which display the spin-crossover transition $^5T_2$(high-spin) $\rightleftharpoons$ $^1A_1$(low-spin). In order to examine the thermally induced spin-crossover transition, we have measured the temperature variation of magnetic susceptibilities and ^{57}Fe Mössbauer spectra of the mixed ligand iron(II) complex [Fe(bpy)(phen)(NCS)$_2$]. Our particular interest is to learn how the mixed coordination of bpy and phen to a central iron(II) ion influences transition temperature, hysteresis effect, and mechanism of spin-transitions.

Experimental

Materials. All reagents were of reagent grade and used without further purification. Tetrakis(pyridine)bis(thiocyanato)iron(II) [Fe(py)$_4$(NCS)$_2$][8)] and bis(pyridine)(1,10-phenanthroline)bis(isothiocyanato)iron(II) [Fe(py)$_2$(phen)(NCS)$_2$][7)] were prepared according to the literature methods.

Preparation. The mixed ligand complex [Fe(bpy)(phen)(NCS)$_2$] was prepared by the following two methods. Method I: A 50 cm^3 solution of 0.49 g (5.00 mmol) KSCN in methanol was added to a 6 cm^3 solution of 0.70 g (2.50 mmol) FeSO$_4\cdot$7H$_2$O in water. The resulting precipitate of K$_2$SO$_4$ was filtered off with a G4 glass filter. To the filtrate was dropwise added a solution of 0.39 g (2.50 mmol) bpy and 0.45 g (2.50 mmol) phen in 50 cm^3 of methanol with vigorous stirring. After the mixed solution was allowed to stand overnight, red purple crystals obtained were filtered, washed with methanol and dried over silica gel. Found: C, 54.7; H, 3.3; N, 15.4%. Calcd for [Fe(bpy)(phen)(NCS)$_2$]: C, 56.70; H, 3.17; N, 16.53%. Method II: A 20 cm^3 solution of 0.31 g (2.00 mmol) bpy in pyridine was slowly added to a 500 cm^3 solution of 1.02 g (2.00 mmol) [Fe(py)$_2$(phen)(NCS)$_2$] in pyridine. The reaction mixture was stirred at 80 °C for 20 h, then evaporated to 50 cm^3 under reduced pressure. After the solution was cooled to room temperature, red purple crystals obtained were collected by filtration, washed with methanol and dried over silica gel. Found: C, 56.3; H, 3.2; N, 15.5%. Calcd for [Fe(bpy)(phen)(NCS)$_2$]: C, 56.70; H, 3.17; N, 16.53%. All manupulations were performed in a nitrogen-filled glovebox to prevent oxidation of iron(II) compounds.

Physical Measurements. The X-ray diffraction powder patterns were taken at room temperature with a Rigaku-

Denki Geigerflex RAD-IIA X-ray diffractometer using graphite-monochromated Cu $K\alpha$ radiation (λ=0.1542 nm). Infrared spectra were recorded on a Hitachi Perkin-Elmer Model 225 grating infrared spectrophotometer using KBr pellets. The calibration of wavenumbers was carried out using polystyrene film. Magnetic susceptibilities were measured in the temperature range between 77 and 300 K by the Bozorth method with $Hg[Co(SCN)_4]$ as a calibrant.[9] The molar susceptibilities were corrected for diamagnetism using the following corrections: Fe^{2+}, −13; bpy, −105; phen, −128; NCS^-, −35 (in units of 10^{-6} cm^3 mol^{-1}).[10,11] Mössbauer spectra were obtained with a 10 mCi ^{57}Co source in Pd foil (The Radiochemical Centre, Amersham, England) using a Wissel constant-acceleration transducer coupled with a Canberra OMEGA-1 multichannel analyzer. The absorber temperature was varied between 77 and 300 K with a Torisha cryostat. The spectra were fitted to Lorentzian curves with an iterative least-square computer program. The isomer shifts were referred to natural iron foil at 293 K.

Results and Discussion

Preparation of Mixed Ligand Complexes. Thermodynamic data are not available for the prediction whether the mixed ligand complex $[Fe(bpy)(phen)(NCS)_2]$ can be synthesized or not. When the target mixed ligand complex is prepared by Method I, one or more than two unfavorable products such as $[Fe(phen)_2(NCS)_2]$ $[Fe(bpy)_2(NCS)_2]$, $[Fe(phen)_3(NCS)_2]$ or $[Fe(bpy)_3](NCS)_2$ are expected to yield under the present experimental conditions. Of these complexes both $[Fe(phen)_3](NCS)_2$ and $[Fe(bpy)_3](NCS)_2$ are easily distinguishable from $[Fe(phen)_2(NCS)_2]$, $[Fe(bpy)_2(NCS)_2]$, and $[Fe(phen)(bpy)(NCS)_2]$ by elemental analysis or Mössbauer spectroscopy. The formation of $[Fe(bpy)_2(NCS)_2]$ is also ignored because it is synthesized only under more rigorous experimental conditions, e.g. by elimination of bpy from $[Fe(bpy)_3](NCS)_2$.[11] One might still suspect that a mixture of $[Fe(bpy)(phen)(NCS)_2]$ and $[Fe(phen)_2(NCS)_2]$ is formed by Method I. Therefore, we undertook Method II in which the pyridine ligands of $[Fe(py)_4(NCS)_2]$ are stepwise replaced by a bidentate phen or bpy. Since the complete substitution of the two remaining pyridine ligands in $[Fe(py)_2(phen)(NCS)_2]$ was supposed to be the most difficult step of the successive substitution reactions, the reaction mixture was heated for a prolonged period (20 h). In spite of somewhat tedious procedures, the successive substitution method employed in Method II was demonstrated to be an excellent method for preparing a variety of mixed ligand complexes. The preparation of some mixed ligand complexes analogous to $[Fe(bpy)(phen)(NCS)_2]$ is in progress in our laboratory.

Identification of Mixed Ligand Complexes. The identity of the mixed ligand complexes prepared by the above two different methods was confirmed by a comparison of the X-ray diffraction powder patterns as well as the infrared spectra. The X-ray diffraction powder patterns of the mixed ligand complex $[Fe(bpy)(phen)(NCS)_2]$ are shown in Fig. 1. The diffraction powder pattern of $[Fe(phen)_2(NCS)_2]$ is also presented for comparative purposes, although the X-ray diffraction data are already reported on this complex.[12] The diffraction pattern of $[Fe(bpy)(phen)(NCS)_2]$ prepared by Method I agrees with that by Method II, indicating that the mixed ligand complexes prepared by the two different methods are identical. The intensities observed for $[Fe(bpy)(phen)(NCS)_2]$ prepared according to Method I and II are appreciably different from those of $[Fe(phen)_2(NCS)_2]$, while the peak positions are very similar to each other. This means that $[Fe(bpy)(phen)(NCS)_2]$ is isomorphous with $[Fe(phen)_2(NCS)_2]$ and the lattice parameters of the former are also quite similar to those of the latter.

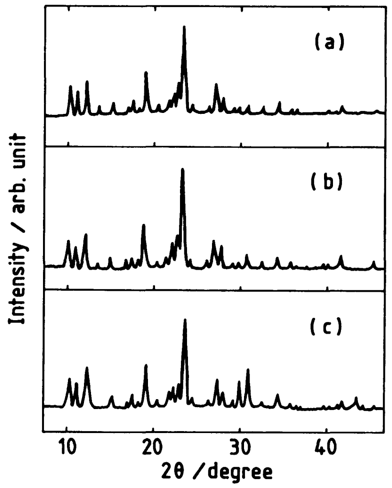

Fig. 1. Comparison of X-ray diffraction powder patterns. (a): $[Fe(bpy)(phen)(NCS)_2]$ prepared by Method I, (b): $[Fe(bpy)(phen)(NCS)_2]$ prepared by Method II, (c) $[Fe(phen)_2(NCS)_2]$.

Table 1. Infrared Absorption Frequencies of Thiocyanato Ligands in $[Fe(bpy)(phen)(NCS)_2]$

Compound	Absorption frequencies/cm^{-1}		
	ν_1(CN str.)	ν_2(SCN bend.)	ν_3(CS str.)
$[Fe(bpy)(phen)(NCS)_2]$[a]	2055	473	800
$[Fe(bpy)(phen)(NCS)_2]$[b]	2055	475	798
$[Fe(phen)_2(NCS)_2]$[c]	2060	(483, 473)	(809)

a) Prepared by Method I. b) Prepared by Method II. c) Taken from 10).

The infrared absorption frequencies observed for [Fe(bpy)(phen)(NCS)$_2$] are listed in Table 1 along with those for [Fe(phen)$_2$(NCS)$_2$]. Three fundamental modes of the thiocyanato ligand are referred to as ν_1(C-N str.), ν_2(N-C-S bend.), and ν_3(C-S str.). The absorption frequencies of these three fundamental modes provide information on whether the central iron(II) ion is coordinated through the nitrogen end or through the sulfur end of the thiocyanato ligand. A comparison of the three frequencies in [Fe(bpy)(phen)(NCS)$_2$] to those in [Fe(phen)$_2$(NCS)$_2$] which are already reported[10)] reveals that the coordination atom of the thiocyanato ligand to the central iron(II) ion is nitrogen in [Fe(bpy)(phen)(NCS)$_2$] prepared by Method I and II. In addition, the range of the absorption frequencies observed for the three fundamental modes clearly indicates that the mixed ligand complexes [Fe(bpy)(phen)(NCS)$_2$] are both in the high-spin state at room temperature. The infrared spectra of mixed ligand complexes are generally very useful in verifying the coordination of different kinds of ligands to a central metal ion. In the present case the absorption positions of bpy are too similar to those of phen to clarify the mixed coordination of both ligands to an iron(II) ion.

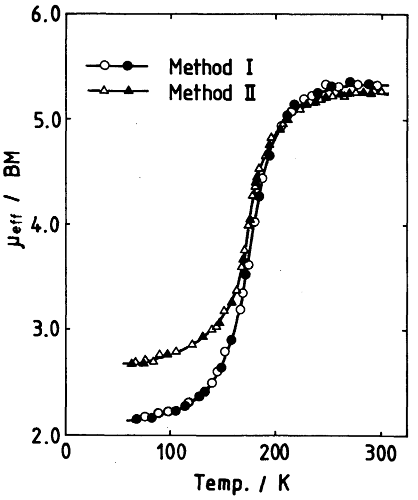

Fig. 2. Temperature dependence of μ_{eff} in [Fe(bpy)(phen)(NCS)$_2$]. ○: Prepared by Method I, △: prepared by Method II. Open and full symbols represent cooling and heating runs respectively.

Influence of Mixed Coordination on Spin-Crossover Behavior. The variation of the effective magnetic moment μ_{eff} of [Fe(bpy)(phen)(NCS)$_2$] with temperature is shown in Fig. 2. The cooling curve of the temperature dependence of the magnetic moment agrees with the heating one and hence no hysteresis effect is observed for [Fe(bpy)(phen)(NCS)$_2$] within experimental errors. The magnetic moments of [Fe(bpy)(phen)(NCS)$_2$] prepared by Method I and II are deflected suddenly at 179 and 175 K, respectively, each of which is here defined as transition temperature. The marked change in magnetic moments within a narrow temperature range indicates that the present mixed ligand complexes do not belong to the spin-equilibrium type but to the spin-transition one. The rather sharp transition is comparable to a reversible quintet-singlet transition observed for [Fe(phen)$_2$(NCS)$_2$],[13)] in which a cooperative transition mechanism is predominant.

The magnetic moments observed at 77 and 293 K are summarized in Table 2 together with the transition temperature. The magnetic moments of [Fe(bpy)(phen)(NCS)$_2$] are rather independent of the preparative methods in the high-temperature range 220 to 300 K. In contrast, the complex prepared by Method I gives lower magnetic moments than that by Method II in the low-temperature range below 120 K. The so-called residual paramagnetism depends on the preparative method employed. The disagreement of the residual paramagnetic moments in the low-temperature range is probably due to the difference in topography of crystalline particles, e.g. boundary surface and size of fine crystals.[14)] In fact, it is reported that an increase of surface area by grinding and doping fine crystals results in an increase of the residual paramagnetic moments in the low-temperature range.[15)] It is to be noted that the residual paramagnetism observed for almost all spin-crossover complexes will be studied because no clearcut explanation has been given to this strange phenomenon. The theoretical interpretation of the temperature dependence of magnetic moments is made more difficult mainly due to the following two reasons: 1)

Table 2. Magnetic Moment and Transition Temperature

Compound	Magnetic moment (BM)		Transition temperature
	High-spin($^5T_2$)	Low-spin($^1A_1$)	K
	293 K	77 K	
[Fe(bpy)(phen)(NCS)$_2$]$^{a)}$	5.26	2.16	179
[Fe(bpy)(phen)(NCS)$_2$]$^{b)}$	5.20	2.79	175
[Fe(phen)$_2$(NCS)$_2$]$^{c)}$	5.17	0.65	174
[Fe(bpy)$_2$(NCS)$_2$]$^{c)}$	5.20	0.94—1.39	215

a) Prepared by Method I. b) Prepared by Method II. c) Taken from 10) and 11).

The $^5T_2$(high-spin) $\rightleftharpoons$ $^1A_1$(low-spin) transition is accompanied by a discontinuous change in metal-ligand distances and 2) the magnetic moments observed in the low-temperature range depend to some extent on the preparative method employed. We believe that the high-spin ($^5T_2$) $\rightleftharpoons$ low-spin ($^1A_1$) transition in [Fe(bpy)(phen)(NCS)$_2$] is thermodynamically of first order, although the present complex does not exhibit any hysteresis effect in the experimental time scale of our magnetic measurements.[16] Of course, the conclusive demonstration should be made by heat capacity measurements, particularly because the transition observed in the magnetic moments is almost discontinuous.

Change in Electronic Structure with Spin-Crossover Transition. The Mössbauer spectra obtained at three different temperatures are shown in Fig. 3. Only the spectra of [Fe(bpy)(phen)(NCS)$_2$] prepared by Method II are given as representative ones because the spectral patterns are similar to those by Method I. A quadrupole-splitting doublet characteristic of iron(II) complexes in the high-spin $^5T_2$ state was observed at 298 K. When the absorber temperature was lowered around 190 K, a quadrupole-splitting doublet assignable to the low-spin $^1A_1$ state began to appear in the Mössbauer spectra. As seen from Fig. 3, the absorption intensity, i.e. the area of the quadrupole splitting doublet is much smaller in the high-spin state than in the low-spin state. This indicates that the recoil-free fraction of the iron nucleus in the high-spin state is extremely small as compared with that in the low-spin state. This should be taken into consideration when the high-spin fraction in [Fe(bpy)(phen)(NCS)$_2$] is estimated from the area of the quadrupole splitting doublet.[17] Thus, almost all the high-spin phase seems to be annihilated in the Mössbauer spectra at 77 K, although there are high-spin molecules of [Fe(bpy)(phen)(NCS)$_2$] at least on the surface of microcrystals and/or at the boundary between magnetic domains. Indeed, measurements of temperature variation in magnetic susceptibilities also show that there exist appreciable paramagnetic species even at 77 K.[18]

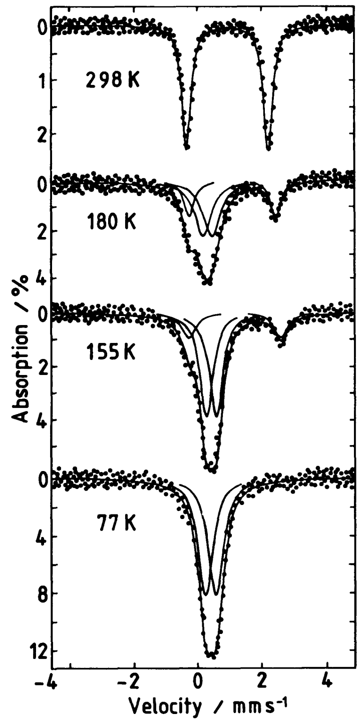

Fig. 3. Mössbauer spectra of [Fe(bpy)(phen)(NCS)$_2$] prepared by Method II.

The Mössbauer parameters obtained at 77 and 293 K are summarized in Table 3, where the parameters of closely related complexes are also listed for comparison. It is noteworthy that the isomer shift as well as the quadrupole splitting decreases on changing from the high-spin to the low-spin state. The thermally induced transition from the high-spin state to the low-spin state is accompanied by an increase in the back donation of 3d electrons to the π^* orbital of the bpy, phen or thiocyanato ligands; the lowering of the 3d electron density around the central iron(II) ion decreases the shielding of the s electron density at the iron nucleus and thereby gives rise to a negative isomer shift. For d^6 iron(II) complexes, the transfer of two electrons from the e_g and t_{2g} orbitals is known to

Table 3. Comparison of Mössbauer Parameters Observed for [Fe(bpy)(phen)(NCS)$_2$] and Related Complexes

Compound	Temp / K	Isomer shift / mms^{-1}	Quadrupole splitting / mms^{-1}
[Fe(bpy)(phen)(NCS)$_2$][a)]	293	0.99_3	2.50_9
	77	0.42_3	0.36_9
[Fe(bpy)(phen)(NCS)$_2$][b)]	293	0.94_5	2.49_6
	77	0.40_1	0.35_4
[Fe(phen)$_2$(NCS)$_2$][c)]	293	1.00	2.67
	77	0.36	0.34
[Fe(bpy)$_2$(NCS)$_2$][c)]	293	1.06	2.15
	77	0.36	0.49

a) Prepared by Method I. b) Prepared by Method II. c) Taken from 10) and 11).

cause a considerable reduction in the metal-ligand bond length. Thus, the cell volume generally contracts on going from the high-spin to low-spin state.[19] On transition from the $^5T_2$ state to the $^1A_1$ state, the tendency of phen or bpy to reduce the electron density on the iron is enhanced by the larger overlap of the iron t_{2g} orbitals and the antibonding π^* orbitals of bpy or phen. Consequently, the increased back donation from the central iron(II) ion to the antibonding π^* orbitals of the ligands causes the shortening of Fe–N bond length.

In the high-spin state, the isomer shifts observed for [Fe(bpy)(phen)(NCS)$_2$] are slightly smaller than those for [Fe(bpy)$_2$(NCS)$_2$] and [Fe(phen)$_2$(NCS)$_2$] while the quadrupole splittings lie between both complexes. On the other hand, in the low-spin state the isomer shifts of [Fe(bpy)(phen)(NCS)$_2$] are somewhat larger than those of [Fe(bpy)$_2$(NCS)$_2$] and [Fe(phen)$_2$(NCS)$_2$]. This suggests that the back donation from the t_{2g} orbitals of the iron(II) ion to the antibonding π° orbitals of bpy, phen, and thiocyanato ligands is smaller in [Fe(bpy)(phen)(NCS)$_2$] than in [Fe(bpy)$_2$(NCS)$_2$] or [Fe(phen)$_2$(NCS)$_2$].

The Mössbauer parameters of [Fe(bpy)(phen)(NCS)$_2$] prepared by Method II are shown as a function of temperature in Fig. 4. In the high-spin temperature range the quadrupole splitting increases with decreasing temperature, while in the low-spin temperature range it is almost independent of temperature. The mixed ligand complex [Fe(bpy)(phen)(NCS)$_2$] prepared by Method I showed a quite similar tendency in the temperature-dependence of its Mössbauer parameters to that prepared by Method II. The temperature variation of the quadrupole splitting in the high-spin temperature range is ascribed to the Boltzmann distribution of 3d electrons among the sublevels in the distorted octahedral ligand field. On the other hand, the isomer shift increases with decreasing temperature both in the high-spin and in the low-spin temperature ranges. This increasing tendency in the isomer shift is due to the so-called second-order Doppler shift. A dramatic change around 180 K in both the isomer shift and the quadrupole splitting demonstrated that the electronic configuration of the central iron(II) ion abruptly changes around this transition temperature. This discontinuous change in Mössbauer parameters is in good accord with the abrupt $^5T_2$(high-spin) $\rightleftarrows$ $^1A_1$-(low-spin) transition observed for the temperature dependence of magnetic moments.

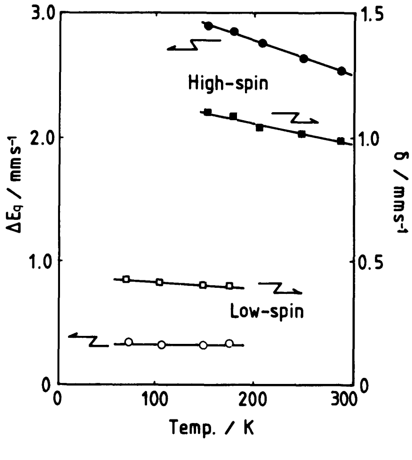

Fig. 4. Temperature dependence of Mössbauer parameters in [Fe(bpy)(phen)(NCS)$_2$] prepared by Method II.

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