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RAPID ELECTRONIC RELAXATION PHENOMENON IN THE TRANSITION BETWEEN $^6A_1$ AND $^2T_2$ STATES

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N,N'-Bis(1-methyl-3-oxobutylidene)ethylenediaminato-1,3-di-4-pyridylpropaneiron(III) tetraphenylborate was synthesized and the temperature dependences of the Mössbauer spectrum and magnetic susceptibility for the compound were measured. The fact that the electronic relaxation between $^6A_1$ and $^2T_2$ states is faster than the lifetime (0.86×10^{-7} s) of the nuclear excited state of an ^{57}Fe Mössbauer atom was confirmed by means of Mössbauer spectroscopy.

The first transition metal compounds with d^4, d^5, d^6, and d^7 electron configurations are usually classified into two categories according to the strength of ligand field against the mean spin-pairing energy, i.e., high- and low-spin compounds. In some cases, however, if the ligand field strength is comparable to mean spin-pairing energy, the complexes exhibit a spin transition as temperature varies. In the present study, new spin crossover iron(III) complex; N,N'-bis(1-methyl-3-oxobutylidene)ethylenediaminato-1,3-di-4-pyridylpropaneiron(III) tetraphenylborate ([Fe(acen)(dpp)](Bph$_4$): H$_2$acen;N,N'-bis(1-methyl-3-oxobutylidene)ethylenediamine, dpp;1,3-di-4-pyridylpropane, and Bph$_4$;tetraphenylborate ion) was synthesized and examined by means of Mössbauer spectroscopy and magnetic susceptibility. It is turned out that the electronic relaxation between $^6A_1$ and $^2T_2$ states is faster than the lifetime of Mössbauer excited state.

The prepartion of the compound was accomplished by the method similar to that of Nishida et al.$^{1)}$ A quadridentate Schiff base (H$_2$acen) used in this study was prepared according to the method of Holm et al.$^{2)}$ The chemical stoichiometry of the complex was confirmed by elemental analysis (Found:C, 73.70;H,6.80;N,6.88%. Calcd for $FeC_{49}H_{52}N_4BO_2$: C,73.97;H,6.59;N,7.04%). Mössbauer spectra were measured using a cobalt-57 source of 10 mCi diffused into a palladium foil. All the spectra were fitted to a Lorentzian line shape using the least square method, and the velocity scale is calibrated with the spectrum for an iron foil at 297 K. Magnetic susceptibility measurement on a polycrystalline sample was carried out by Faraday method. HgCo(NCS)$_4$ was used as a reference and the effective magnetic moment was obtained from the relation $\mu_{eff}=2.84\sqrt{\chi_M T}$, where χ_M is the molar susceptibility after applying diamagnetic corrections.

The temperature profiles of the effective magnetic moment and reciprocal molar susceptibility for [Fe(acen)(dpp)](Bph$_4$) are shown in Fig. 1. The values of the effective magnetic moment of this complex increase gradually from 2.53 B.M. at 78 K to 5.70 B.M. at 308 K. The changes of enthalpy (ΔH) and entropy (ΔS) accompanying with a spin transition are evaluated by using the following equation; lnK=-ΔH/RT + ΔS/R, where K is a equilibrium constant obtained from the relation K=x/(1-x). The high-spin population (x) at a certain temperature was obtained assuming a simple additive property in magnetic susceptibilities. The changes of the enthalpy and entropy are calculated to be 8.8x10^3 Jmol^{-1}and 45.1 JK^{-1}mol^{-1}, respectively. The magnetic contribution to the entropy change is expected to be Rln3= 9.1 JK^{-1}mol^{-1} for the $^6A_1$ - $^2T_2$ process. This indicates that the spin transition is strongly coupled with the phonon system as suggested by Sorai and Seki.$^{3)}$

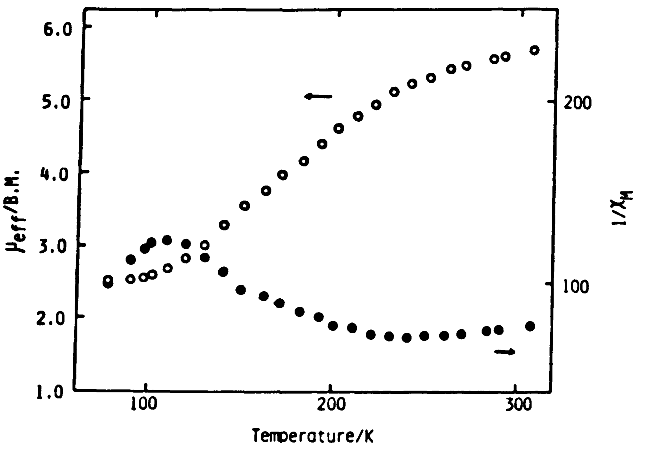

Fig. 1 Temperature dependences of the effective magnetic moment (○) and reciprocal molar susceptibility (●) for [Fe(acen)(dpp)](Bph$_4$).

The separation energy (E) between zero-point levels of the low- and high-spin states is evaluated by means of the theoretical calculation of the temperature dependence of effective magnetic moments. Considering the ratio (C) of the molecular vibrational partition functions in the two spin states, the temperature dependence of the effective magnetic moment can be expressed as$^{4)}$

$$\mu_{eff}^2 = \frac{0.75g^2 + 8x^{-1}(1-\exp(-3x/2)) + 105C\exp(-(1+(E/\zeta))x)}{1 + 2\exp(-3x/2) + 3C\exp(-(1+(E/\zeta))x)}$$

where ζ is the one-electron spin orbit coupling constant, and x=ζ/kT. In this calculation, the value of logC was evaluated from the equilibrium constant and determined to be 1.88, and the experimental g-value (g=2.14) obtained by EPR spectrum at 80 K was used. The best fit values were calculated to be E= 536 cm^{-1} and =163 cm^{-1} by applying the least square method. Ewald et al. reported the values of E ranging from 100 to 1000 cm^{-1} for several tris(N,N'-disubstituted-dithiocarbamato)iron(III) complexes.$^{4)}$

Figure 2 shows the temperature dependence of the Mössbauer spectra for this complex. Only one quadrupole doublet is observed over the whole temperature range. The resonance lines corresponding to low-spin iron(III) below 180 K have a narrow fwhm (fwhm: full width at half-maximum). Resonance lines corresponding to high-spin iron(III) have a broad fwhm. The spectrum at 330 K shows broad lines, but the resonance lines characteristic of high-spin iron(III) are expected at a temperature higher than 330 K. The peak asymmetry of the spectra at high temerature results from the magnetic relaxation (spin-spin relaxation) of high-spin iron(III), because the iron is coordinated with bulky ligands like acen and dpp. A superposition of the quadrupole doublets of two spin states over the temperature range of the spin transition (180-270 K) is usually expected in the Mössbauer spectra. However, only one quadrupole doublet with a broad fwhm is observed in this temperature range. As shown in Fig. 3, the temperature dependences of isomer shift and quadrupole splitting between 90 and 165 K exhibit typical behavior of the low-spin iron (III) state. These two Mössbauer parameters over the temperature range of 180-261 K change up to the values of high-spin iron(III), and vary in proportion to the abundance of the high-(or low-) spin state. This indicates that the relaxation time of one form (a low-spin state) to the other form (a high-spin state) is faster than the Mössbauer lifetime ($0.86X10^{-7}$ s) and that a nucleus "sees" an average state of a high- and low-spin states. Namely, the Mössbauer spectra of this complex are explained by assuming a rapid electronic relaxation phenomenon between the two spin states.

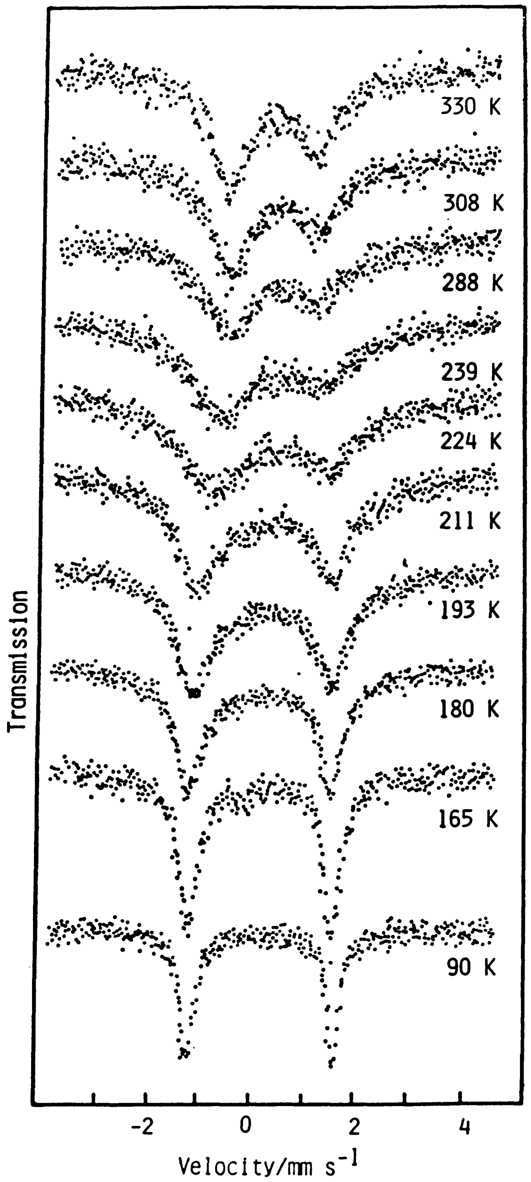

Fig. 2 Mössbauer spectra of [Fe(acen)(dpp)](Bph$_4$) at various temperatures.

The spectra were fitted by the time-dependent Hamiltonian for a nucleus in an environment where the principal component of an axially symmetric electric field gradient jumps at random between low-spin and high-spin states.[5)]

$$H = H_0 + (1 + f(t))\frac{\Delta_{hs}}{12}(3I_z^2 - I^2) + (1 - f(t))\frac{\Delta_{ls}}{12}(3I_z^2 - I^2)$$

where a random function of time f(t) is ±1, Δ_{hs} and Δ_{ls} are the quadrupole splittings characteristic of high-spin and low-spin species, respectively. The calculations were tried for the spectra at 193 K and 180 K because the spectra above 211 K are asymmetric. The high-spin population (x) obtained by the magnetic measurement (x=0.456 at 193 K and x=0.385 at 180 K) were used. The relaxation times ($\tau_{hl}=7.1\times10^{-8}$ s at 193 K and $\tau_{hl}=7.6\times10^{-8}$ s at 180 K) are calculated for the spectra using the least square method.

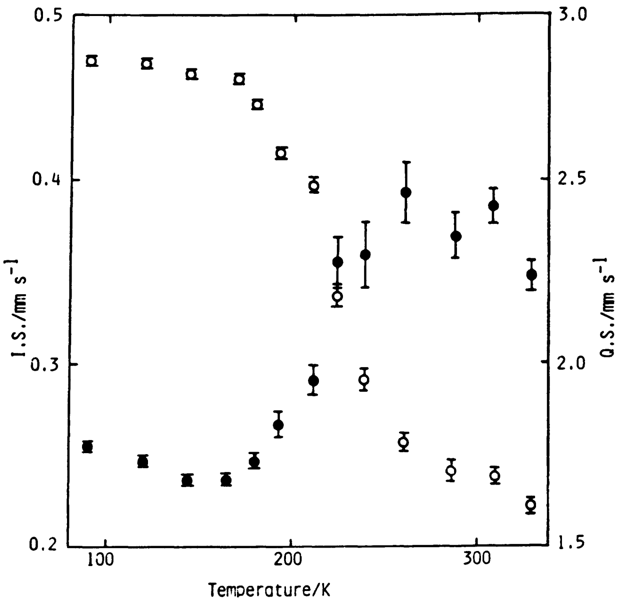

Fig. 3 Temperature dependences of the isomer shift (●) and quadrupole splitting (○) for [Fe(acen)(dpp)](Bph$_4$).

The rapid electronic relaxation phenomenon of spin crossover systems has been seen in the cases of tris (N,N'-disubstituted-dithiocarbamato)iron(III) complexes[6,7)] ($^6A_1$ and $^2T_2$) and TaFeS$_2$[8)] ($^5T_2$ and $^1A_1$). The present work can provide a new example (N$_4$O$_2$ coordination) of spin crossover complex which shows very rapid electronic relaxation phenomenon. The study to make clear whether this rapid electronic relaxation phenomenon is due to intermolecular or intramolecular mechanism is currently under way in our laboratory.

References

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