Spin-Equilibrium Behavior in Solution of an Iron(III) Complex [Bis-[3-(3-methoxysalicylideneamine)propyl]amino-*O,N,N',N'',O'*](pyridine)-iron(III) Tetraphenylborate

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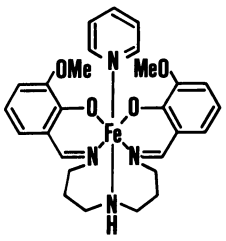
Synopsis. The title iron(III) complex with a spin equilibrium between high-spin(S=5/2) and low-spin(S=1/2) has been investigated by means of the temperature dependences of the magnetic susceptibilities (the Evans ^{1}H NMR technique), the electronic spectra, and the cyclic voltammetry. The pure electronic spectra for high-spin and low-spin species were evaluated from the observed electronic spectra and the equilibrium constants obtained from the magnetic data. The electron-transfer entropy for the $Fe^{3+}+e \rightarrow Fe^{2+}$ process(ΔS_{et}) was obtained as 205 $JK^{-1}mol^{-1}$ from the temperature dependence of the cyclic voltammogram.

We have previously reported the syntheses and characterizations of new families of spin-equilibrium mononuclear and binuclear iron(III) complexes, in which the spin-equilibrium behavior in the solid states has been investigated by the temperature dependences of the magnetic susceptibilities and the Mössbauer spectra.[1,2]

In this study, the spin-equilibrium behavior in the solution state of the title complex, whose schematic structure is shown in the drawing, has been investigated by means of the temperature dependences of the magnetic susceptibilities (the Evans ^{1}H NMR technique), the electronic spectra, and the cyclic voltammetry.



Experimental

Synthesis. The title complex [Fe(py)L][BPh_4] was prepared by the general method reported previously,[1] in which 3-methoxy-salicylaldehyde instead of salicylaldehyde was used for this complex. Found: C, 71.52; H, 6.13; N, 6.26%. Calcd for $FeC_{51}H_{52}N_4O_4B$: C, 71.93; H, 6.15; N, 6.58%. Mp 167—169 °C.

Physical Measurements. Magnetic susceptibility measurements in dichloromethane solution were performed by the Evans ^{1}H NMR method,[3] using a JEOL JNM-FX 100 spectrometer, where the Me_4Si was used as the reference compound. The magnetic susceptibility was corrected by the diamagnetism of the component atoms by the use of Pascal's constants. The effective magnetic moment was calculated by means of the equation; $\mu_{eff}=2.828\sqrt{\chi_A T}$. The temperature dependence of the electronic spectra in a dichloromethane solution was recorded with a Hitachi spectrophotometer model 340, according to the procedure of the literature.[4] Variable temperature cyclic voltammetric measurements were obtained with a three-electrode system using a Hokuto Denki HB-103 linear scanner and a HA-201 potentiostat with a Rika Denki model RW-11 XY-recorder. The working electrode was a platinum button, and a platinum wire served as the counter electrode. A commercial saturated calomel electrode(SCE) was used as the reference electrode and was separated from the bulk of the solution by a fritted glass bridge with the same solvent and supporting electrolyte (tetrabutylammonium perchlorate). The cell was cooled by circulating cold methanol. The temperature of the solution was monitored by means of a Yokogawa-Hokushin Denki digital multi-thermometer, type 2572, and was kept constant within ±0.2 °C during the measurement.

Results and Discussion

The [Fe(py)L][BPh_4] complex showed a striking thermochromism both in the solid and in the solution, changing its color from black in the solid and violet in the solution at the ambient temperature to green at the temperature of liquid nitrogen, which is characteristic of a spin equilibrium. The temperature dependence of the electronic spectra of the complex was measured in several organic solvents (dichloromethane, chloroform, acetonitrile, acetone, methanol, and ethanol) in order to examine the solvent effect on the spin-equilibrium behavior. Among the temperature dependences of the electronic spectra measured in various organic solvents, the spectrum measured in dichloromethane showed the most drastic thermochromic behavior with a set of isosbestic points, so that the spin-equilibrium behavior of the complex was thereafter studied in the dichloromethane solution by the use of variable-temperature techniques of magnetic susceptibility, electronic spectrum, and cyclic voltammetry.

The magnetic susceptibilities were measured in a dichloromethane solution by the Evans ^{1}H NMR method.[3] The effective magnetic moments at various temperatures are as follows (μ_B (K)): 5.55 (281), 5.50 (276), 5.45 (271), 5.33 (267), 5.24 (260), 5.07 (254), 4.98 (250), 4.85 (244), 4.60 (239), 4.44 (235). The μ_{eff} decreases from 5.55 μ_B at 281 K to 4.44 μ_B at 235 K, indicating a spin equilibrium between high-spin(S=

5/2) and low-spin(S=1/2). The equilibrium constant, defined as K=[high-spin]/[low-spin], was calculated from the expression: $K=(\mu_{eff}^2-\mu_{LS}^2)/(\mu_{HS}^2-\mu_{eff}^2)$, where μ_{HS} and μ_{LS} are the limitting high-spin and low-spin magnetic moments respectively. The value of μ_{HS} was fixed at 5.92, the spin-only value for the ^{6}A state. The value of μ_{LS} was taken as 2.0. The equilibrium constant, K, can be related to the entropy and enthalpy differences between high-spin and low-spin species by means of Eq. 1:

$$RT\ln K = \Delta H - T\Delta S \quad (1)$$

A plot of log K vs. T^{-1} is shown in Fig. 1. The data gives a straightline plot of log K vs. T^{-1}, with a ΔH value of 19.6 kJ mol^{-1} and ΔS value of 82.8 JK^{-1} mol^{-1}. The ΔH value is similar to the values reported for the spin-equilibrium iron(III) complexes $[Fe(X\text{-salmeen})_2]^+$ and $[Fe(X\text{-sal})_2trien]^+$,[5,6] where X-salmeen denotes the tridentate ligand derived from salicylaldehyde and N-methylethylenediamine and where (X-sal)$_2$trien denotes the hexadentate ligand derived from salicylaldehyde and bis(3-aminopropyl)amine. The ΔS value is somewhat larger than the values reported for the $[Fe(X\text{-salmeen})_2]^+$ and $[Fe(X\text{-sal})_2trien]^+$ complexes.

The temperature dependence of the electronic spectrum of the [Fe(py)L][BPh$_4$] complex in the dichloromethane solution is shown in Fig. 2. The spectrum changes with the set of isosbestic points at 420, 620, and 820 nm, suggesting a thermal equilibrium between two different electronic isomers, i.e., high-spin and low-spin species. At a single wavelength, the absorbance, A, is given by Eq. 2, where ε_{obsd} is the observed molar extinction coefficient, and where ε_{LS} and ε_{HS} are the molar extinction coefficients of the low-spin and high-spin species respectively:

$$A = \varepsilon_{obsd}([LS]+[HS]) = \varepsilon_{LS}[LS]+\varepsilon_{HS}[HS] \quad (2)$$

Equation 2 can be written as Eq. 3, using the equilibrium constant K=[HS]/[LS]:

$$(K+1)\varepsilon_{obsd} = \varepsilon_{LS} + K\varepsilon_{HS} \quad (3)$$

Therefore, a plot of $(K+1)\varepsilon_{obsd}$ vs. K gives the values of ε_{HS} from the slope and ε_{LS} from the intercept, where the values of K were estimated from the magnetic moments and where seven K values below 273 K were used. The electronic spectra of the pure high-spin and low-spin species were determined from this calculation; they are shown in Fig. 2 as dotted lines. The calculated electronic spectrum of the high-spin species exhibits two absorption maxima, at 450 and 560 nm, with the molar extinction coefficients of 3400 and 3400 mol^{-1} dm^3 cm^{-1}, while that of the low-spin species exhibits an absorption maximum at 670 nm, with the molar extinction coefficient of 3300 mol^{-1} dm^3 cm^{-1}.

The electrochemical reduction of the [Fe(py)L][BPh$_4$] complex involves a reversible one-electron transfer attributable to an Fe(III)/Fe(II) redox process. The half-wave potential for the reduction is observed at 0.018 V, and the peak separation, $E_{pa}-E_{pc}$, is 67 mV at 287 K. The electrochemical reduction was investigated in a dichloromethane solution as a function of the temperature between 287 and 257 K. A linear plot of $E_{1/2}$ vs. T was observed; it is shown in Fig. 3. The entropy change(ΔS_{et}) for the electrochemical reduction may be calculated from Eq. 4:[7]

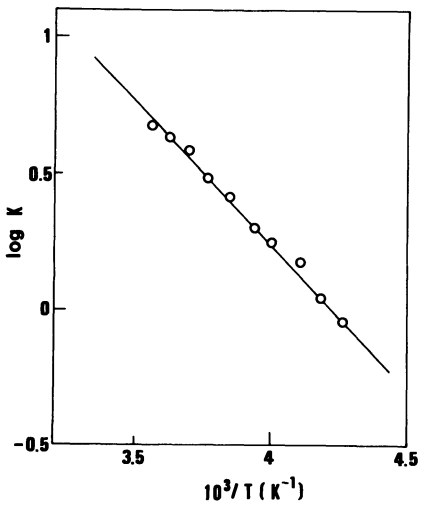


Fig. 1. A plot of log K vs. T^{-1} for [Fe(py)L][BPh$_4$], where K was calculated by the equation of $K=(\mu_{eff}^2-\mu_{LS}^2)/(\mu_{HS}^2-\mu_{eff}^2)$, and μ_{HS}=5.92 and μ_{LS}=2.00 were used.

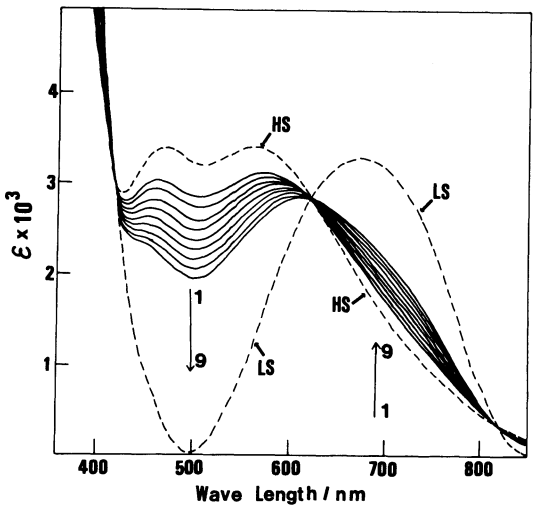


Fig. 2. Temperature dependence of the electronic spectrum for [Fe(py)L][BPh$_4$] in dichloromethane solution; 1(281.7 K), 2(277.7 K), 3(273.2 K), 4(268.2 K), 5(263.2 K), 6(258.2 K), 7(253.2 K), 8(248.2 K), 9 (243.2 K). The pure high-spin and low-spin spectra are shown as dotted lines.

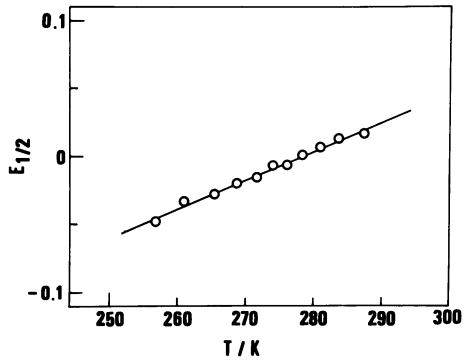


Fig. 3. A plot of $E_{1/2}$ vs. T for [Fe(py)L][BPh_4], where $E_{1/2}$ is relative to Saturated Calomel Electrode(SCE).

$$\Delta S_{et} = nF(\Delta E_{1/2}/\Delta T) \quad (4)$$

where n is the number of electrons transferred and where F is the Faraday constant. From Eq. 4, the value of ΔS_{et} was evaluated to be 205 $JK^{-1}mol^{-1}$. Kadish and his co-workers studied the electron-transfer properties of the spin-equilibrium iron(III) complexes and reported that the ΔS_{et} values varied from 88 to 146 $JK^{-1}mol^{-1}$ for [Fe(X-salmeen)$_2$]$^+$ and from 67 to 75 $JK^{-1}mol^{-1}$ for [Fe(X-sal)$_2$trien]$^+$.[8] Therefore, the ΔS_{et} value for the present complex is considerably larger than those for the [Fe(X-salmeen)$_2$]$^+$ and [Fe(X-sal)$_2$trien]$^+$.

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References

1) N. Matsumoto, S. Ohta, C. Yoshimura, A. Ohyoshi, S. Kohata, H. Okawa, and Y. Maeda, *J. Chem. Soc., Dalton Trans.*, **1985**, 2575.
2) S. Ohta, C. Yoshimura, N. Matsumoto, H. Okawa, and A. Ohyoshi, *Bull. Chem. Soc. Jpn.*, **59**, 155 (1986).
3) D. F. Evans, *J. Chem. Soc.*, **1959**, 2003.
4) M. Sugimoto, M. Nonoyama, T. Ito, and J. Fujita, *Inorg. Chem.*, **22**, 950 (1983).
5) R. H. Petty, E. V. Dose, M. F. Tweedle, and L. J. Wilson, *Inorg. Chem.*, **17**, 1064 (1978).
6) R. A. Binstead, J. K. Beattie, T. G. Deway, and D. H. Turner, *J. Am. Chem. Soc.*, **102**, 6442 (1980).
7) K. M. Kadish, *Phys. Bioinorg. Chem. Ser.*, **2**, 230 (1982).
8) T. Zhu, C. Su. Schaeper, B. K. Lemke, L. J. Wilson, and K. M. Kadish, *Inorg. Chem.*, **23**, 4345 (1984), and the references cited therein.