Synthesis and Characterization of a Chloro-bridged Binuclear Iron(III) Complex

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Synopsis. A chloro-bridged binuclear iron(III) complex $[Fe_2ClL](BPh_4)$, where $[H_4L]$ and BPh_4^- denote *N,N,N′,N′*-tetrakis(3-salicylideneaminopropyl)ethylenediamine and tetraphenylborate, respectively, was prepared and characterized by elemental analysis, electrical conductivity, Mössbauer spectrum, and cryomagnetic data. The magnetic susceptibility data of the complex was analyzed by the Heisenberg model on the basis of a binuclear structure $\hat{H}=-2J\hat{S}_1\cdot\hat{S}_2$ ($S_1=S_2=5/2$), leading to an antiferromagnetic interaction parameter of $J=-3.9\,cm^{-1}$.

Chloro-bridged iron(III) complexes are rare, although a number of oxo-bridged iron(III) complexes are well known.[1] In this study, a chloro-bridged binuclear iron(III) complex $[Fe_2ClL](BPh_4)$ is reported, where $[H_4L]$ and BPh_4^- denote a decadentate binucleating ligand *N,N,N′,N′*-tetrakis(3-salicylideneaminopropyl) ethylenediamine and tetraphenylborate, respectively. The complex was characterized by elemental analysis, electrical conductivity, Mössbauer spectrum, and cryomagnetic data, and their physical properties were compared with those of the corresponding mononuclear complex chloro[*N,N*-bis(3-salicylideneaminopropyl) methylaminato] iron(III).

Experimental

Physical Measurements. Elemental analyses (C, H, N) were performed by Mr. Shinichi Miyazaki at the Technical Service Center of Kumamoto University, and an analysis of Cl was carried out by the Fajans method. Melting points were measured on a Yanagimoto micro melting point apparatus and were uncorrected. Electrical conductivity measurements were carried out on a Denki Kagaku AOC-10 type digital conductometer at *ca.* 10^{-3} mol dm^{-3} in methanol or *N,N*-dimethylformamide. The ^1H NMR spectrum was recorded on a JEOL MH 100 spectrometer, where the solvent used was chloroform-*d* and shift measurements were made relative to tetramethylsilane. Magnetic susceptibilities were obtained by the Faraday method in a temperature range between liquid nitrogen temperature and room temperature, according to the literature.[2] The susceptibility was corrected for the diamagnetism of the component atoms by the use of Pascal's constants. An effective magnetic moment was calculated using $\mu_{eff}=2.828\sqrt{\chi_A T}$, where χ_A is the magnetic susceptibility per iron atom. The Mössbauer spectroscopy was effected by using an instrument described elsewhere.[3] An isomer shift is reported with respect to the centroid of the spectrum of an iron foil enriched with ^{57}Fe at 295 K. This was also used as a standard material for a velocity calibration.

Syntheses. Binucleating Ligand [H4L]: *N,N,N′,N′*-Tetrakis(3-aminopropyl)ethylenediamine hexahydrobromide was prepared according to a method described in the literature.[4] A mixture of *N,N,N′,N′*-tetrakis(3-aminopropyl)ethylenediamine hexahydrobromide, salicylaldehyde, and triethylamine with a mole ratio of 1:4:6 in ethanol was stirred on a water bath. Yellow crystals precipitated and were collected and recrystallized from a mixture of chloroform and ethanol. Found: C, 71.58; H, 7.48; N, 11.93%. Calcd for $C_{22}H_{28}N_6O_4$: C, 71.56; H, 7.44; N, 11.92%. Mp 112 °C, ^1H NMR ($CDCl_3$) δ=1.7 [8H, m, $4CH_2$], 2.4 [12H, t, $6CH_2$], 3.5 [8H, t, $4CH_2$], 6.6—7.3 [16H, m, $4C_6H_4$], 8.2 [4H, s, 4CH=N].

[Fe2ClL](BPh4). The ligand $[H_4L]$ (10 mmol) and anhydrous iron(III) chloride (20 mmol) were mixed in 100 cm^3 of methanol. To the mixture was added triethylamine (40 mmol) and the resulting solution was warmed at 50 °C for 30 min and then filtered. To the filtrate was added a solution of sodium tetraphenylborate (20 mmol) in 30 cm^3 of methanol. This was warmed at 50 °C for 1 h to yield fine black crystals. These were collected, washed with methanol, and dried *in vacuo*. Found: C, 67.75; H, 6.06; N, 7.22; Cl, 3.24%. Calcd for $C_{66}H_{68}N_6BClO_4Fe_2$: C 67.91; H, 5.87; N, 7.20; Cl, 3.04%. Mp 255 °C (decomp), Λ_M 47.4 Scm^2 mol^{-1} (DMF).

Chloro[N,N-bis(3-salicylideneaminopropyl)methylaminato]-iron(III) [FeClL′]. The mononuclear chloro complex [FeClL′], used as a reference complex, was prepared according to a method described in the literature.[5] Found: C, 56.75; H, 5.80; N, 9.50%. Calcd for $C_{21}H_{25}N_3ClO_2Fe$: C, 56.97; H, 5.69; N, 9.49%. Mp 219 °C, Λ_M 0.0 Scm^2 mol^{-1}(MeOH).

Results and Discussion

The molar electrical conductance of the complex was 47.4 Scm^2 mol^{-1} in *N, N*-dimethylformamide,[6] indicating that the complex has a formula of $[Fe_2ClL]^+(BPh_4)^-$, although this value is slightly smaller than the expected value (65—90 Scm^2 mol^{-1}) of a 1:1 electrolyte in DMF.[7] The molar electrical conductance of the mononuclear complex shows that the complex is uncharged and has a formula of [FeCLL′].

The magnetic moment of the mononuclear complex [FeClL′] is independent of the temperature over the temperature range studied within the experimental error (*ca.* 5.9 BM), typical of a high spin (S=5/2) iron(III) complex. On the other hand, the magnetic moment of $[Fe_2ClL](BPh_4)$ gradually increased from 4.8 BM at 90 K to 5.6 BM at 300 K. Plots of χ_A and $1/\chi_A$ *vs.* temperature for [FeClL′] and $[Fe_2ClL](BPh_4)$ are shown in Fig. 1. The magnetism of the mononuclear chloro complex [FeClL′] obeys the Curie law, while that of the complex $[Fe_2ClL](BPh_4)$ obeys the Curie-Weiss law ($\chi_A=C/(T+\theta)$) with a Weiss constant of θ=50 K. This suggests antiferromagnetic interaction between iron (III) centers. The Mössbauer spectrum of $[Fe_2ClL](BPh_4)$ at 296 K showed a doublet with parameters of IS=0.380, QS=0.741, Γ=0.370 mms^{-1}, typical of a high-spin (S=5/2) center.

The magnetic susceptibilities of the complex $[Fe_2ClL](BPh_4)$ were analyzed by the Heisenberg model

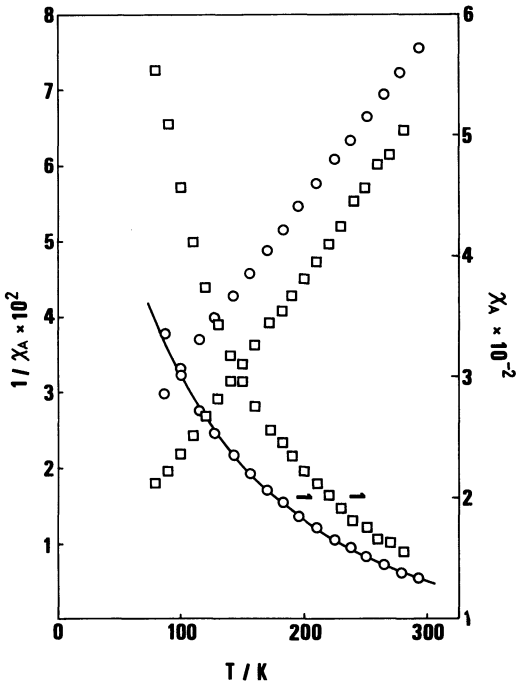

Fig. 1. Plots of χ_A and $1/\chi_A$ *vs.* temperature for [FeClL'] (□) and [Fe_2ClL](BPh_4) (○), where the solid line of χ_A *vs.* T plot for [Fe_2ClL](BPh_4) represents the theoretical curve of Eq. 1 with the parameters of g=2.00, J=−3.9 cm^{-1}, and p=0.015.

on the basis of a binuclear structure. The magnetic susceptibility per iron atom of a binuclear structure (S_1=S_2=5/2) is given by Eq. 1,

$$\chi_A = \frac{Ng^2\beta^2}{kT}\frac{55+30x^{10}+14x^{18}+5x^{24}+x^{28}}{11+9x^{10}+7x^{18}+5x^{24}+3x^{28}+x^{30}}(1-p) + \frac{35Ng^2\beta^2}{12kT}p \quad (1)$$

where x=exp(−J/kT) and p is the amount of magnetically dilute ferric impurity which possibly coexists with the dimer. Other symbols have their usual meanings. An isotropic g value of 2.00 was assumed, and the best fit to the data gave J=−3.9 cm^{-1} and

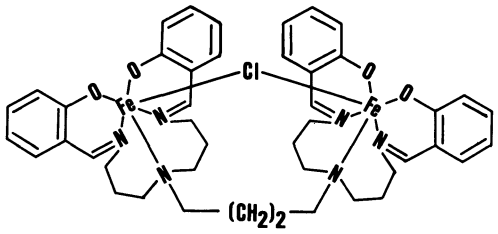

Fig. 2. A proposed structure for [Fe_2ClL]$^+$.

p=0.015. A theoretical χ_A *vs.* T curve using the above parameters is represented as a solid line in Fig. 1. On the basis of the electrical conductance and the magnetic property, it can be concluded that the complex [Fe_2ClL](BPh_4) assumes a binuclear structure with a chloro-bridge as shown in Fig. 2.

A number of oxo-bridged binuclear iron(III) complexes have been known and the antiferromagnetic interaction parameters vary from *ca.* −10 cm^{-1} to *ca.* −100 cm^{-1},[1] indicating that the antiferromagnetic interaction of the chloro-bridged complex is considerably smaller than those of the oxo-bridged complexes.

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