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The Synthesis, Magnetic, and Spectroscopic Properties of Binuclear Iron(III) Complexes Bridged by Pyrazine, 1,1′-Tetramethylenebis(imidazol), or Bis(pyridine) Compounds Exhibiting a Spin-Equilibrium Behavior

Shoichi Ohta, Chikako Yoshimura, Naohide Matsumoto, Hisashi Okawa,[†]
and Akira Ohyoshi*
Department of Synthetic Chemistry, Faculty of Engineering, Kumamoto University,
Kurokami 2-39-1, Kumamoto 860
[†]Department of Chemistry, Faculty of Science, Kyushu University,
Hakozaki, Higashi-ku, Fukuoka 812

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Five binuclear iron(III) complexes bridged by pyrazine, 1,1′-tetramethylenebis(imidazol), or bis(pyridine) compounds with the formula of $[\mathrm{LFe(Bge)FeL}](\mathrm{BPh_4})_2$ have been prepared, and their spin-equilibrium behavior between high-spin($S=5/2$) and low-spin($S=1/2$) states has been investigated by means of the temperature dependences of the magnetic susceptibilities and the electronic spectra, where Bge denotes pyrazine, 1,1′-tetramethylenebis(imidazol), 4,4′-bipyridine, 4,4′-ethylenebis(pyridine), or 4,4′-vinylenebis(pyridine), L=bis(3-salicylideneaminopropyl)amine, and $\mathrm{BPh_4^-}$=tetraphenylborate. The pyrazine complex is low-spin, while the bis(imidazole) and the bis(pyridine) complexes showed a spin-equilibrium between high-spin and low-spin states, accompanied by a striking thermochromism in both the solids and solutions.

Previously, we have shown that a series of iron(III) complexes with the general formula of $[\mathrm{FeXL}]^{n+}$ (n=0,1) are a new family among spin-equilibrium iron(III) complexes.[1)] In these complexes, the pentadentate ligand (L=bis(3-salicylideneaminopropyl)amine) is kept constant and the spin-state of iron(III) depends on the position of the sixth ligand X in the spectrochemical series; i.e., the chloro and azido complexes are high-spin, the complexes with imidazole or pyridine derivatives are spin-equilibrium, and the cyano complex is low-spin.

A number of mononuclear iron(III) complexes with spin-equilibrium, including our complexes, have been known.[1—9)] However, to our knowledge, no binuclear iron(III) complex with spin-equilibrium has been reported. In this study, binuclear iron(III) complexes bridged by pyrazine, 1,1′-tetramethylenebis(imidazol), or bis(pyridine) compounds with the formula of $[\mathrm{LFe(Bge)FeL}](\mathrm{BPh_4})_2$ were prepared, and their spin-equilibrium behavior was clarified by means of the temperature dependence of the magnetic susceptibilities and electronic spectra, in order to investigate the influence of the formation of binuclear species or the nature of the bridging ligand on the spin state of iron(III). The spin-equilibrium behavior of the binuclear complexes $[\mathrm{LFe(Bge)FeL}](\mathrm{BPh_4})_2$ is compared with that of the corresponding mononuclear complexes $[\mathrm{FeXL}](\mathrm{BPh_4})$. The schematic structures of the mononuclear $[\mathrm{FeXL}]^{n+}$ (n=0,1) and binuclear $[\mathrm{LFe(Bge)FeL}]^{2+}$ iron(III) complexes, along with the abbreviations used in this text, are shown in Fig. 1.

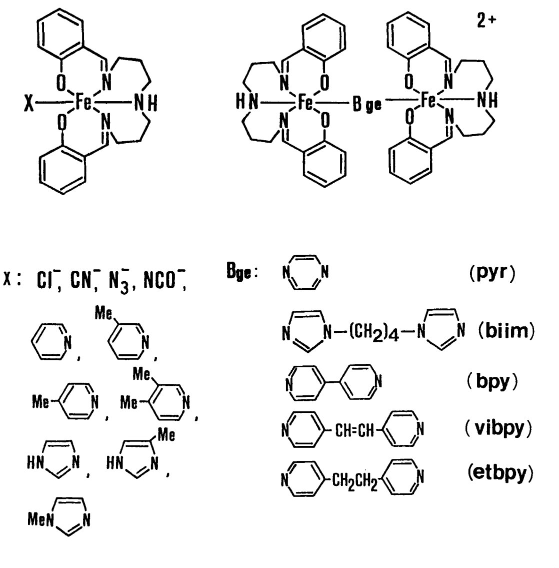

Fig. 1. Structures of mononuclear $[\mathrm{FeXL}]^{n+}$ (n=0,1) and binuclear $[\mathrm{LFe(Bge)FeL}]^{2+}$ iron(III) complexes: Bge=pyrazine(pyr), 1,1′-tetramethylenebis(imidazol) (biim), 4,4′-bipyridine(bpy), 4,4′-vinylenebis(pyridine) (vibpy), and 4,4′-ethylenebis(pyridine)(etbpy), where the abbreviations of bridging ligands Bge are given in parentheses.

Experimental

Physical Measurements. The melting points were measured on a Yanagimoto micromelting-point apparatus and uncorrected. The elemental analyses were performed by Mr. Shinichi Miyazaki at the Technical Service Center of Kumamoto University. The 100 MHz ^{1}H NMR spectrum was recorded on a JEOL MH 100 spectrometer; the solvent used was $\mathrm{CDCl_3}$, and the shift measurements were made relative to $\mathrm{SiMe_4}$. The thermogravimetric analysis was carried out on a Shimadzu TGC-20 microthermobalance at the heating rate of 5 °C min^{-1}, using ca. 20 mg of the sample. The electrical-conductivity measurements were carried out on a Denki Kagaku AOC-10 apparatus in dichloromethane solution on ca. 10^{-3} mol dm^{-3}. The reflectance spectra of the ground samples were measured on a Shimadzu UV-260 apparatus at the ambient temperature.

The temperature dependence of the electronic spectra in a dichloromethane solution was recorded with a Hitachi spectrophotometer 323, where the cell temperature was controlled by a circulating bath with a thermostat and where the sample temperature was monitored by means of a Yokogawa-Hokushin Denki digital multithermometer, Type 2572, and was kept constant within ±0.1 °C during the measurement. The magnetic susceptibilities were measured by the Faraday method in the temperature range from liquid nitrogen temperature to room temperature, according to a procedure reported previously.[10]

Syntheses. **1,1′-Tetramethylenebis(imidazol) Dihydrate.** The bis(imidazole) was prepared according to the method in the literature[11] and was identified by means of elemental analysis, its mp, its ^{1}H NMR spectrum, and thermogravimetric analysis. Found: C, 53.16; H, 7.88; N, 24.80%. Calcd for $C_{10}H_{14}N_4 \cdot 2H_2O$: C, 53.08; H, 8.02; N, 24.76%. mp 56—71 °C (Ref. 58—75 °C), ^{1}H NMR ($CDCl_3$) δ=1.70 (4H, m, CH_2), 1.80 (4H, s, H_2O), 3.80 (4H, m, CH_2), 7.10 (6H, q, aromatic), mass loss 15.9 wt% (55—130 °C), Calcd for $2H_2O$:15.9 wt%.

[FeClL]. The chloro iron(III) complex as a starting material was prepared according to the method reported previously.[1]

Binuclear Iron(III) Complexes [LFe(Bge)FeL](Bph$_4$)$_2$. The binuclear iron(III) complexes bridged by pyrazine, 1,1′-tetramethylene-bis(imidazol), or bis(pyridine) compounds were obtained by mixing stoichiometric amounts of [FeClL] and the bridging ligand in a mole ratio of 2:1 and by then adding sodium tetraphenylborate to provide a counter anion, where pyrazine, 1,1′-tetramethylenebis(imidazol), 4,4′-bipyridine, 4,4′-ethylenebis(pyridine), and 4,4′-vinylenebis(pyridine) were used as bridging ligands. The syntheses of all the binuclear complexes are practically the same, so only the synthesis of the 4,4′-bipyridine complex [LFe(bpy)FeL]$(BPh_4)_2$ will be described in detail as an example. To a solution of [FeClL] (2 mmol) in 50 cm^3 of methanol was added a solution of 4,4′-bipyridine (1 mmol). The mixture was warmed at 60 °C for 10 min and then filtered. The filtrate was added to a solution of sodium tetraphenylborate (2.5 mmol) in 10 cm^3 of methanol. The resulting crystals were filtered, washed with methanol and diethyl ether, and dried in vacuo.

Results and Discussion

Binuclear iron(III) complexes [LFe(Bge)FeL]$(BPh_4)_2$ were prepared by mixing stoichiometric amounts of [FeClL] and the bridging ligand (Bge) in methanol and by then adding a slight excess of sodium tetraphenylborate. The elemental analytical data, melting points, molar electrical conductances in 10^{-3} mol dm^{-3} dichloromethane solutions, and colors in the solids and solutions at the ambient temperature and at the temperature of liquid nitrogen are summarized in Table 1. As shown in Table 1, the bis(pyridine) complexes showed a striking thermochromism both in the solids and solutions. On the other hand, the pyrazine complex showed no thermochromism in the solid state, and its green color is characteristic of low-spin complexes.[1]

The temperature dependences of the magnetic moments for the binuclear iron(III) complexes [LFe(Bge)FeL]$(BPh_4)_2$ are shown in Fig. 2, where the magnetic moment per iron is given. As could be

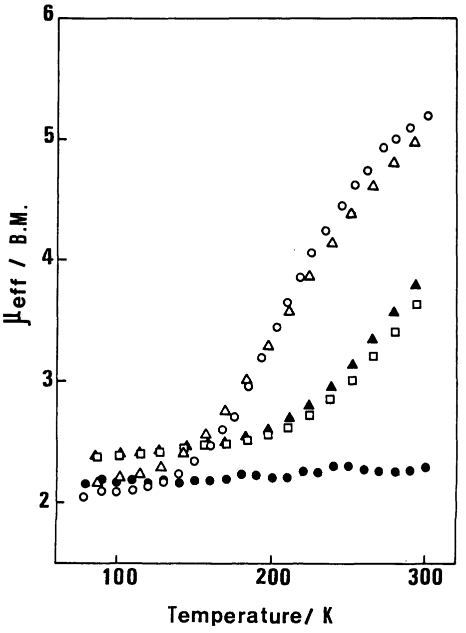

Fig. 2. Temperature dependences of effective magnetic moments for binuclear iron(III) complexes [LFe(Bge)FeL]$(BPh_4)_2$, Bge: pyr (●), biim (○), bpy(△), vibpy(□), etbpy(▲).

Table 1. Elemental Analytical Data, Melting Points, Molar Electrical Conductances,[a] and Colors[b] at *ca.* 80 and 300 K in the Solids and Solutions[c]

Complex	C(%) Found(Calcd)	H(%) Found(Calcd)	N(%) Found(Calcd)	Mp θ_m/°C	a	Color solid	soln
[LFe(pyr)FeL]$(BPh_4)_2$	73.52(73.42)	6.01(6.03)	7.43(7.45)	153—157	49.1	G-G	V-V
[LFe(biim)FeL]$(BPh_4)_2$	72.70(72.87)	6.18(6.24)	8.71(8.67)	205—207	45.5	DV-G	V-BG
[LFe(bpy)FeL]$(BPh_4)_2$	74.04(74.44)	6.05(5.99)	6.96(7.08)	200—205	45.7	DV-G	V-DG
[LFe(vibpy)FeL]$(BPh_4)_2$	74.64(74.73)	6.23(6.02)	6.88(6.97)	235—240	60.8	DV-G	V-G
[LFe(etbpy)FeL]$(BPh_4)_2$	74.56(74.64)	6.18(6.14)	6.94(6.96)	213—215	66.2	DV-G	V-G

a) Electrical conductance in ca. 10^{-3} mol dm^{-3} dichloromethane solutions/S mol^{-1} cm^2. b) Colors at 300 K (left) and 80 K (right); V, violet; DV, dark violet; BG, blue green; DG, dark green; G, green. c) In a dichloromethane solution.

predicted from its green color, the pyrazine complex [LFe(pyr)FeL](BPh$_4$)$_2$ is essentially low-spin, because the magnetic moment (ca. 2.2 BM) is in the expected range for low-spin ($S=1/2$) iron(III) complexes and is independent of the temperature. On the other hand, the magnetic moments for the bis(imidazole) and the bis(pyridine) complexes showed temperature dependence, indicating that the complexes exhibit a spin-equilibrium between high-spin($S=5/2$) and low-spin ($S=1/2$) states. Since the spin-transition for these complexes takes place over a wide range of temperatures, the complexes, on the basis of König's criterion,[12] can be classified as forming a continuous type of spin-equilibrium complexes. The magnetic moments for the bis(imidazole) and 4,4′-bipyridine complexes [LFe(biim)FeL](BPh$_4$)$_2$ and [LFe(bpy)FeL](BPh$_4$)$_2$ increase gradually from a low-spin value (ca. 2.2 BM) at 80 K to a nearly high-spin value (ca. 5.3 BM) at 300 K, indicating that the spin-transition from the low-spin state to the high-spin state is almost completed in the temperature range studied. For the other two bis(pyridine) complexes, [LFe(etbpy)FeL](BPh$_4$)$_2$ and [LFe(vibpy)FeL](BPh$_4$)$_2$, the magnetic moments gradually increase from 2.3 BM at 80 K to ca. 3.7 BM at 300 K, suggesting that the spin-transition seems to be completed at a temperature higher than 300 K.

It is of interest to compare the magnetic behavior of the binuclear complexes [LFe(Bge)FeL](BPh$_4$)$_2$ with that of the corresponding mononuclear complexes [FeXL](BPh$_4$). The magnetic behavior of the bis(imidazole) complex [LFe(biim)FeL](BPh$_4$)$_2$ can be compared with that of the mononuclear complexes with imidazole derivatives [FeXL](BPh$_4$) (X=im, 1-meim, 2-meim). The bis(imidazole) complex showed the spin-transition between ca. 130 and 300 K, while [FeimL](BPh$_4$) and [Fe1-meimL](BPh$_4$) are high-spin complexes between 80 and 300 K, and [Fe2-meimL](BPh$_4$) showed the spin-transition between ca. 130 and 300 K.[1] The magnetic behavior of the bis(pyridine) complexes [LFe(Bge)FeL](BPh$_4$)$_2$ (Bge=bpy, etbpy, vibpy) can be compared with that of the mononuclear complexes [FeXL](BPh$_4$) (X=py, 3-mepy, 4-mepy, 3,4-dmepy). The μ_{eff} vs. T curves for the [FeXL](BPh$_4$) complexes (X=py, 3-mepy, 4-mepy, 3,4-dmepy) are roughly compatible with those for the [LFe(etbpy)FeL](BPh$_4$)$_2$ and [LFe(vibpy)FeL](BPh$_4$)$_2$ complexes, but are obviously different from that for [LFe(bpy)FeL](BPh$_4$)$_2$.

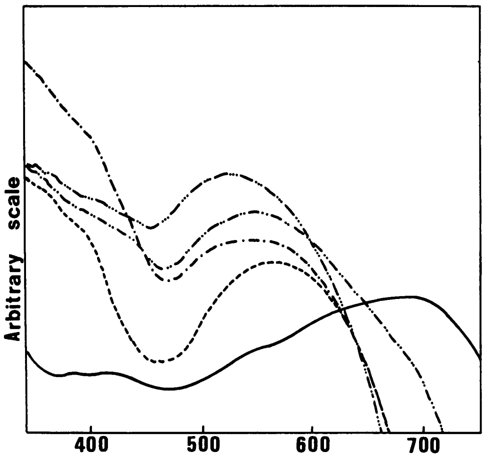

Fig. 3. Reflectance spectra for binuclear iron(III) complexes [LFe(Bge)FeL](BPh$_4$)$_2$, Bge: pyr(——), biim(—⋯⋯—), bpy(—⋯—), vibpy(—·—), etbpy(----).

The reflectance spectra for the binuclear complexes at the ambient temperature are shown in Fig. 3. The complexes exhibit an intense broad band in visible region. The pyrazine complex has the absorption maximum at 680 nm, while the bis(imidazole) and the bis(pyridine) complexes have the maxima around 550 nm. The results from the reflectance spectra are compatible with those from the magnetic moments at the ambient temperature.

The temperature dependence of the electronic spectra was measured in dichloromethane solutions. All the binuclear complexes except for the pyrazine complex showed thermochromic behavior. The pyrazine complex exhibits a green color in the solid and a violet color in the dichloromethane solution. The pyrazine complex showed no thermochromism in a solution, probably because the complex decomposes to form a penta-coordinated complex with the formula of [FeL](BPh$_4$). Figure 4 shows the temperature dependence of the spectrum for [LFe(bpy)FeL](BPh$_4$)$_2$. The spectral patterns of the bis(pyridine) complexes are similar to each other and to those of the corresponding mononuclear complexes with pyridine derivatives.[1] At 16 °C, the spectrum for [LFe(bpy)FeL](BPh$_4$)$_2$ exhibits two absorptions, at 430 and 490 nm, with extinction coefficients of 8500 and 7100 dm^3 mol^{-1} cm^{-1} attributable to the charge-transfer bands. With a lowering in the temperature, the absorption at 430 nm decreases in intensity and that at 490 nm shifts to a higher wavelength, accompanied by a decrease in the intensity. The temperature dependence of the electronic spectrum is probably due to the spin-equilibrium between high-spin and low-spin states, as is known for the well-characterized spin cross-over complexes.[1–9] The spectral changes are associated with two pseudo-isosbestic points at 400 and 510 nm, in which the latter is gradually displaced from 510 nm to a higher wavelength with a lowering in the temperature. The disagreement of the isosbestic points is attributable to the partial dissociation of 4,4′-bipyridine from the complex. When the spectrum was measured after having been left overnight, the absorbance was reduced by almost one

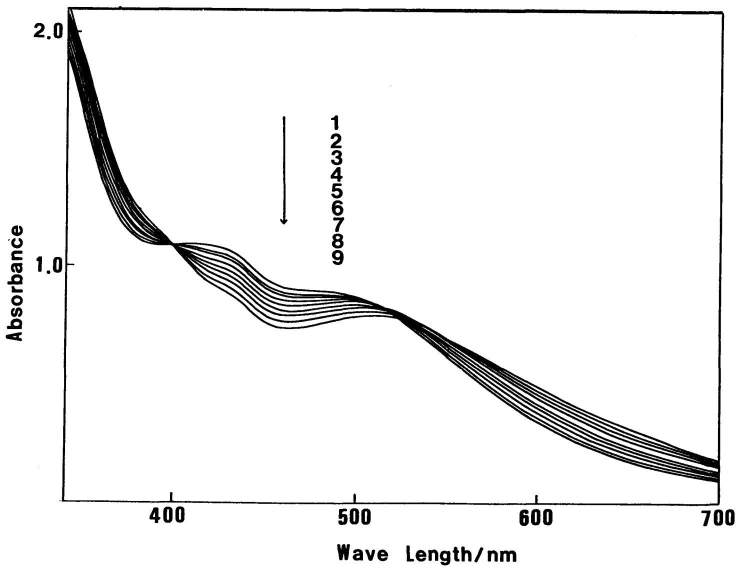

Fig. 4. Temperature dependence of electronic spectrum for $[LFe(bpy)FeL](BPh_4)_2$ in 1.257×10^{-4} mol dm^{-3} dichloromethane solution: (**1**: 16.0 °C, **2**: 13.0 °C, **3**: 10.0 °C, **4**: 7.0 °C, **5**: 4.0 °C, **6**: 1.0 °C, **7**: −2.0 °C, **8**: −5.0 °C, **9**: −8.0 °C).

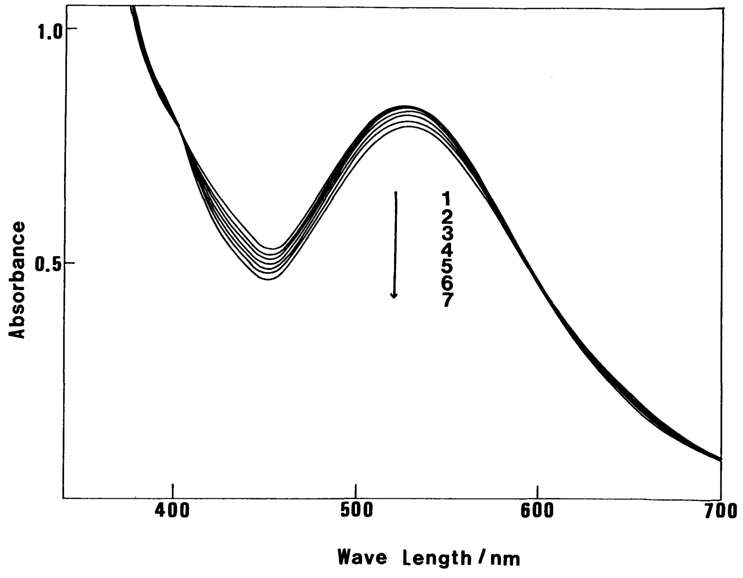

Fig. 5. Temperature dependence of electronic spectrum for $[LFe(biim)FeL](BPh_4)_2$ in 1.158×10^{-4} mol dm^{-3} dichloromethane solution: (**1**: 16.0 °C, **2**: 10.4 °C, **3**: 6.8 °C, **4**: 3.1 °C, **5**: −1.0 °C, **6**: −7.0 °C, **7**: −9.5 °C).

half, while the spectral pattern is consistent with that of the sample measured immediately after the preparation. Figure 5 shows the temperature dependence of the spectrum for the bis(imidazole) complex $[LFe(biim)FeL](BPh_4)_2$. The spectrum exhibits a band at 530 nm, which decreases in intensity with a lowering of the temperature. The spectrum changes with a set of isosbestic points at 400 and 595 nm.

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