Synthesis and Magnetic Properties of Binuclear Iron(III) Complexes Containing Photoisomerization Ligand

Shinya Hayami,* Katsuya Inoue, Susumu Osaki,† and Yonezo Maeda††
Institute for Molecular Science, Myodaiji, Okazaki 444-8585
†*Radioisotope Center, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-0053*
††*Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-0053*

(Received July 3, 1998; CL-980499)

Binuclear iron(III) spin-crossover complex $[Fe_2(salten)_2(az)](BPh_4)_2$ (az=azobis(4-pyridine)) was synthesized and characterized by X-ray single-crystal diffraction, Mössbauer spectra, magnetic susceptibilities and electronic spectra. This complex contains the ligand which is able to photoisomerize as a bridging ligand. The complex exhibited the spin-crossover behavior depending on temperature in solution and solid state. Mössbauer measurements indicated that the complex exhibited rapid spin-equilibrium behavior at room temperature.

Magnetic properties of spin-crossover complexes depend on extrinsic factors such as temperature or pressure.[1] The spin-crossover iron(II) complexes show the low-spin state to the high-spin state transition by the irradiation of green light. Usually, the high-spin state is stable at low temperature. This phenomenom is explained on the basis of light-induced excited spin state trapping; LIESST.[2] Recently, ligand-driven light-induced spin changes (LD-LISC) in the spin-crossover iron(II) complexes have been reported.[3] The spin transition occurs by varying the ligand field strength under photochemical *cis-trans* isomerization of the ligand. The phenomenon has observed by using 4-styrylpyridine derivatives at relatively high temperatures. One of the advantages of this LD-LISC effect is that the spin transition in iron(II) complexes induce by molecular crystal structure or packing changes.

In this paper, we report the structure, magnetic property and electronic spectra of binuclear spin-crossover iron(III) complex with ligand containing a diazo moiety.

The axial ligand az=azobis(4-pyridine) was prepared as described previously.[4] The preparation of the complex was accomplished by the method similar to that of Matsumoto et al.[5]

The temperature dependence of the magnetic susceptibility was investigated in the solid state on a Quantum Design MPMS5S SQUID susceptometer/magnetometer. The temperature dependence of the effective magnetic moment was investigated in 5000 Oe (Figure 1). The magnetic moment of the complex gradually increased with the temperature increases from ca. 2.2 μ_B (for S=1/2) at 200 K to 4.3 μ_B at 350 K. This result indicates spin-equilibrium state ($S=1/2 \leftrightarrow S=5/2$) achieved at 350 K.

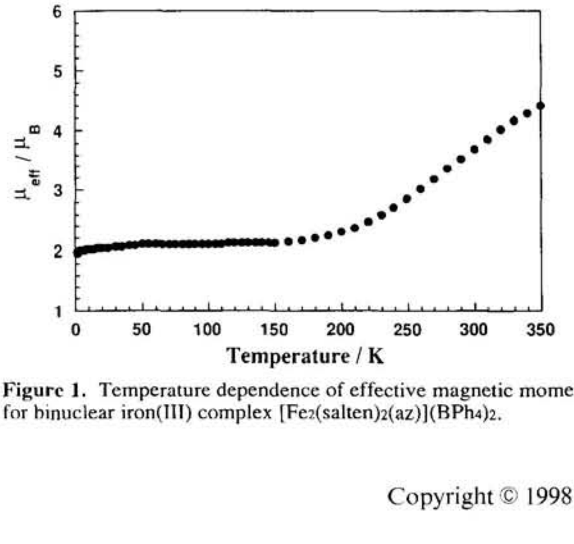

Figure 1. Temperature dependence of effective magnetic moments for binuclear iron(III) complex $[Fe_2(salten)_2(az)](BPh_4)_2$.

The variable temperature Mössbauer spectra of the complex are shown in Figure 2. The typical absorption for low-spin iron(III) (δ=0.25 mms^{-1} relative to α-Fe and ΔE_q=1.53 mms^{-1}) is observed at 95 K. On the other hand, the spectrum of the complex shows only a narrow quadrupole-split doublet (δ=0.28 mms^{-1} and ΔE_q=0.89 mms^{-1}) at 298 K. The Mössbauer parameters and the magnetic moment (μ_{eff}=3.70 μ_B) suggest that the rapid spin-equilibrium between high- and low-spin states achieved in the complex at 298 K. The spectra for rapid intercrossing between high- and low-spin states have been theoretically examined by Maeda et. al.[6]

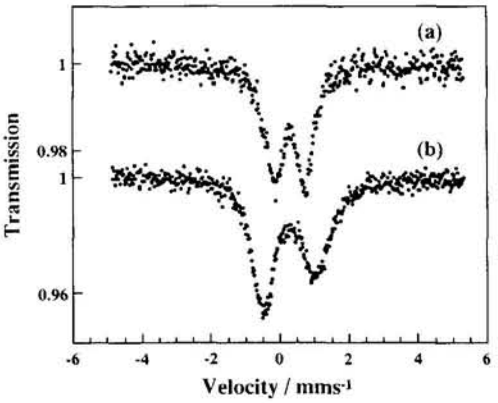

Figure 2. Mössbauer spectra for $[Fe_2(salten)_2(az)](BPh_4)_2$ (a) at 293 K and (b) at 95 K.

The ORTEP view of the complex is shown in Figure 3.[7] The binuclear iron(III) complex is bridged by az ligand. The diazo (N=N) moiety of the complex sits on an inversion center of crystal unit in *trans* geometry. Fe-O (1.89 Å) and Fe-N (2.03 Å) bond distances are intermediate between the typical values of the bond distances for high-spin complexes Fe-O (1.91 Å) and Fe-N (2.16 Å) and low-spin complexes Fe-O (1.88 Å) and Fe-N (1.98 Å).

The temperature dependence of the electronic spectra was measured in acetonitrile solution. The complex showed thermochromic behavior. The photo-induced electronic spectra were measured in acetonitrile solution at room temperature with a high-pressure mercury lamplight 300 nm obtained by using of a 34U band-path filter and are shown in Figure 4. The spectral

Copyright © 1998 The Chemical Society of Japan

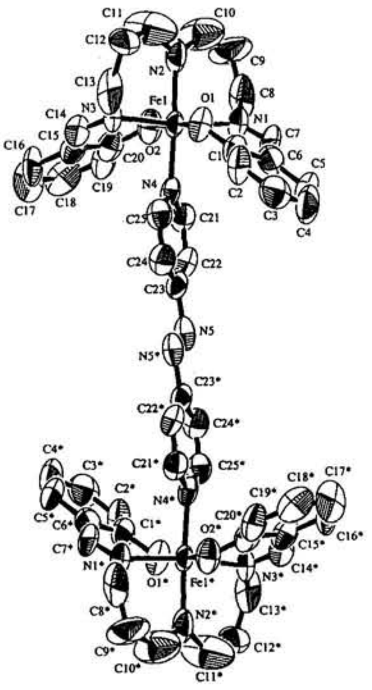

Figure 3. ORTEP view of $[Fe_2(salten)_2(az)](BPh_4)_2$ showing 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

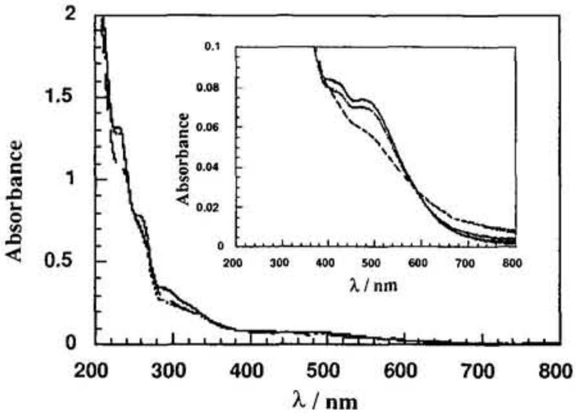

Figure 4. Absorption spectra at room temperature of $[Fe_2(salten)_2(az)](BPh_4)_2$ in acetonitrile solution before (—) and after(----) irradiation at λexc=300 nm, and 3 days after discontinuance of the irradiation(-—). Insert: corresponding absorbance evolution in the LMCT band area.

patterns changed reversibly by light irradiation on the band at 240 and 500 nm. The pattern changes are similar to those of the temperature dependence. In the spectrum after irradiation, the absorption at 430 nm increases in intensity and that at 480 nm decreases in intensity relatively.

The KBr disk containing the complex was irradiated at room temperature until the photostationary state was reached. The initial and final spectra are shown in Figure 5. The absorptions at 320 and 580 nm of the initial spectrum are assigned to *trans* isomer of diazo moiety and LMCT in spin-equilibrium state, respectively. On the other hand, final spectrum with the absorption bands at 360 and 530 nm shows that irradiated samples change to *cis* isomer and to expected high-spin species.

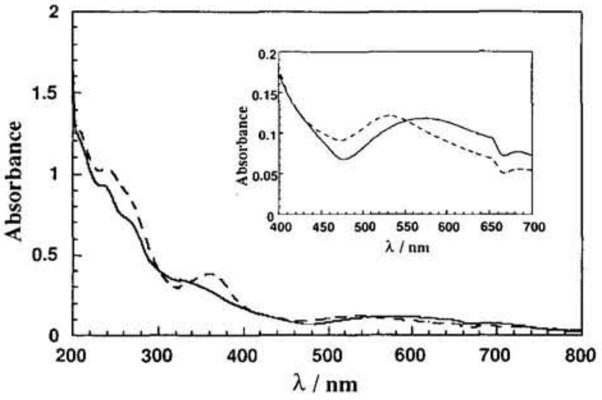

Figure 5. Absorption spectra at room temperature of $[Fe_2(salten)_2(az)](BPh_4)_2$ dispersed in KBr before (—) and after (----) irradiation at λ_{exc}=300 nm. Insert: corresponding absorbance evolution in the LMCT band area.

Binuclear iron(III) complex $[Fe_2(salten)_2(az)](BPh_4)_2$ exhibited rapid spin-equilibrium behavior at room temperature. The absorption spectrum for the complex with photoisomerization az ligand changes between before and after the irradiation with a set of isosbestic points at 350 and 580 nm reversible in solution and irreversible in solid state. The spectra patterns may exhibit photochromic spin transition behavior in solid state.

References and Notes

1 P. Gütlich, *Struct. Bonding*, **44**,83 (1981); E. König, G. Ritter, and S. K. Kulshreshtha, *Chem. Rev.*, **4**, 19 (1985); Y. Maeda and Y. Takashima, Comments *Inorg. Chem.*, **7**, 44 (1988); C. Roux, J. Zarembowitch, J.-P. Itié, A. Polian, and M. Verdaguer, *Inorg. Chem.*, **35**, 574 (1996); J. A. Real, E. Andrés, M. C. Muñoz, M. Julve, T. Granier, A. Bousseksou, and F. Varret, *Science*, **268**, 265 (1995).

2 P. Gütlich and A. Hauser, and H. Spiering, *Angew. Chem., Int. Ed. Engl.*, **33**, 2024 (1994); S. Schenker, A. Hauser, and R. Dyson, *Inorg. Chem.*, **35**, 4676 (1996).

3 C. Roux, J. Zarembowitch, B. Gallois, T. Granier, and R. Claude, *Inorg. Chem.*, **33**, 2273 (1994); M.-L. Boillot, C. Roux, J.-P. Audiére, A. Dausse, and J. Zarembowitch, *Inorg. Chem.*, **35**, 3975 (1996).

4 D. A. Baldwin, A. B. P. Lever, and R. V. Parish, *Inorg. Chem.*, **8**, 107 (1969).

5 N. Matsumoto, S. Ohta, C. Yoshimura, A. Ohyoshi, S. Kohata, H. Okawa, and Y. Maeda, *J. Chem. Soc., Dalton Trans.*, **1985** 2575; S. Ohta, C. Yoshimura, N. Matsumoto, H. Okawa, and A. Ohyoshi, *Bull. Chem. Soc. Jpn.*, **59** 155 (1986).

6 Y. Maeda, H. Oshio, K. Toriumi, and Y. Takashima, *J. Chem. Soc., Dalton Trans.*, **1991**, 1227.

7 Crystal data for $[Fe_2(salten)_2(az)](BPh_4)_2$: $C_{98}H_{94}O_4N_{10}B_2Fe_2$, FW=1609.20, monoclinic, space group $P2_1/c$ (#14), a=16.422(7), b=16.005(6), c=16.565(8) Å, β=108.47(3)°, V=4129(2) Å^3, Z=2, D_{calc}=1.294 gcm^{-3}, Data collection at 293 K with a Rigaku AFC-7R diffractometer; R=0.075 and R_W=0.060 for 2485 observations ($I>3.00\sigma(I)$).