# Thermal and Pressure Induced Spin Crossover of a Novel Iron(III) Complex with a Tripodal Ligand Involving Three Imidazole Groups

Yukinari Sunatsuki, Masafumi Sakata, Susumu Matsuzaki, Naohide Matsumoto*, and Masaaki Kojima[†]

Department of Chemistry, Faculty of Science, Kumamoto University, 2-39-1, Kurokami, Kumamoto 860-8555
[†]*Department of Chemistry, Faculty of Science, Okayama University, 3-1-1, Tsushima-naka, Okayama 700-8530*

A novel spin crossover Fe(III) complex, $[Fe(H_3L)](ClO_4)_3$·(4-fim)·H_2O (H_3L = tris[2-(((imidazol-4-yl)methylene)amino)-ethyl]amine, 4-fim = 4-formylimidazole), was synthesized and the crystal structure was determined at 293 K. Cryomagnetic measurements revealed a two-step spin conversion and a pressure induced spin crossover was observed.

The phenomenon of spin crossover (SC) between low-spin (LS) and high-spin (HS) states, which is one of the most spectacular examples of molecular bistability, can be induced by external perturbations such as temperature, pressure, and light irradiation.[1] Spin crossover compounds with a long-lived metastable state and large hysteresis are of current interest for application to memory and display devices.[2] Such interesting spin crossover compounds have been found for Fe(II) complexes with a limited number of ligands such as pyridine, pyrazole, triazole, and tetrazole derivatives.[3] In order to develop this important field, spin crossover complexes with novel ligand systems must be synthesized. In this study, we report a novel spin crossover Fe(III) complex with a tripodal ligand involving three imidazole groups.
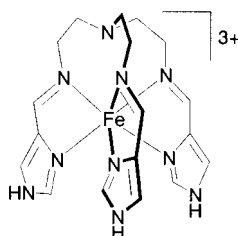
The tripod-type hexadentate ligand H_3L (H_3L = tris[2-(((imidazol-4-yl)methylene)amino)ethyl]amine) was prepared by mixing tris(2-aminoethyl)amine and 4-formylimidazole in 1:3 molar ratio in water, the ligand solution being used without isolation for the synthesis of the Fe(III) complex. A complex with the chemical formula $[Fe(H_3L)](ClO_4)_3$·(4-fim)·H_2O (4-fim = 4-formylimidazole) was obtained as dark red prismatic crystals by mixing the ligand solution, $FeCl_3$ and $NaClO_4$ in water and standing the resulting solution overnight.[4] The molar conductivity was 301 S mol^{-1} cm^2 in water, this value being consistent with a 1:3 electrolyte. The IR spectrum at ambient temperature showed two bands assignable to the C=N stretching vibrations of the Schiff-base ligand at 1625 and 1633 cm^{-1}, together with the band of the C=O vibration of 4-formylimidazole at 1678 cm^{-1} and the characteristic bands for ClO_4^- ion around 1100 cm^{-1}. The color of the powdered sample was dark brown and dark purple at ambient and liquid nitrogen temperatures, respectively, suggesting a thermal spin crossover.

The sample was cooled quickly to 2 K from room temperature and the magnetic susceptibility was measured on increasing

the temperature under an external magnetic field of 1 T.[5] The plots of $\chi_A T$ vs T are given in Figure 1. The curve is divided into three parts, (a) 2–150 K, (b) 150–250 K, and (c) 250–300 K. In part (a) 2–150 K, the $\chi_A T$ value of 0.41 cm^3 K mol^{-1} is almost constant and is in the range expected for a low-spin Fe(III) (S = 1/2). In part (b) 150–250 K, the $\chi_A T$ value increases gradually and reaches 2.44 cm^3 K mol^{-1} at 250 K, showing a bend in the curve. The $\chi_A T$ value of 2.44 cm^3 K mol^{-1} at 250 K is close to the value expected for 1:1 coexistence of a high-spin Fe(III) (S = 5/2) and a low-spin Fe(III) (S = 1/2) species. Above 250 K in part (c), $\chi_A T$ increases gradually due to the spin-transition of the second Fe site from low- to high-spin Fe(III). The $\chi_A T$ value of 3.40 cm^3 K mol^{-1} at 300 K, the highest temperature measured, suggests that the spin conversion of the second Fe(III) site is not complete, with 51% of the second site having converted to the high-spin state, under the assumption of the spin-only values of S = 1/2 and S = 5/2. This two-step spin conversion is consistent with the existence of two crystallographic Fe(III) sites, as described later. The second run of the magnetic measurements was carried out on lowering the temperature from 300 to 2 K immediately after the first run, and $\chi_A T$ vs T is also plotted in Figure 1. The curve is smooth and there is no indication of the two-step spin conversion. The disagreement between the first and second runs indicates the small frozen-in effect due to a weak cooperative effect.
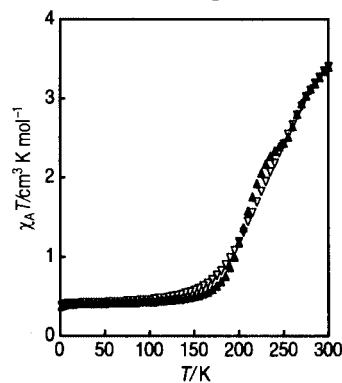
Figure 1. The magnetic behavior in the form of the $\chi_A T$ vs T plot. The first run (▲) was measured on elevating the temperature. The second run (▽) was measured on lowering the temperature.

The crystal structure was determined by single-crystal X-ray analysis at 293 K.[6] The systematic extinction of the X-ray diffraction data suggests that the space group is either $C2/c$ or Cc. When the space group $C2/c$ was assumed, more than 50 reflections gave significant differences between the observed and calculated intensities. The space group $C2/c$ was therefore rejected and the space group Cc was chosen. The crystal structure consists of two protonated $[Fe(H_3L)]^{3+}$ (Fe1 and Fe2) species, six perchlorate ions as the counter anions, two 4-formylimidazoles,
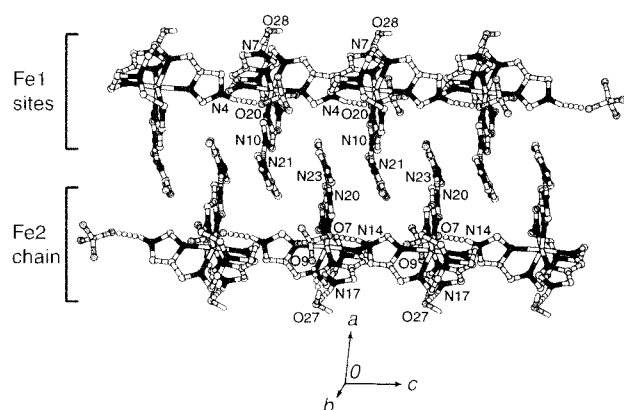
Figure 2. One dimensional network structure for Fe2 site running along the *c*-axis constructed by hydrogen-bonds. Fe–N distances [Å]: Fe(1)–N(2) = 2.13(1), Fe(1)–N(3) = 2.15(1), Fe(1)–N(5) = 2.07(1), Fe(1)–N(6) = 2.13(1), Fe(1)–N(8) = 2.09(1), Fe(1)–N(9) = 2.07(1); Fe(2)–N(12) = 2.03(1), Fe(2)–N(13) = 2.07(1), Fe(2)–N(15) = 2.08(1), Fe(2)–N(16) = 2.14(1), Fe(2)–N(18) = 2.05(1), Fe(2)–N(19) = 2.10(1). N–Fe–N angles [deg]: N2–Fe1–N3 = 77.0(5), N5–Fe1–N6 = 78.0(5), N8–Fe1–N9 = 77.8(5), N12–Fe2–N13 = 75.5(5), N15–Fe2–N16 =74.8(5), N18–Fe2–N19 = 76.3(5).

and two water molecules in the unique unit. Each Fe(III) ion assumes a similar octahedral coordination environment with the N_6 donor atoms of three Fe–N(imine) and three Fe–N(imidazole) bonds. The average Fe–N distance of 2.11 Å for Fe1 is longer than the 2.08 Å for Fe2. The N–Fe–N angles for Fe1 are closer to octahedral than those for Fe2. Another distinct difference between the Fe1 and Fe2 sites is found in the intermolecular hydrogen bonding network. Three imidazole nitrogen atoms of each Fe(III) complex are hydrogen-bonded to a perchlorate ion, a water molecule, and 4-formylimidazole with distances of N(4)···O(20) = 2.81(1), N(7)···O(28) = 2.84(1), and N(10)···N(21) = 2.79(1) Å for Fe1 and of N(14)···O(7) = 2.86(1), N(17)···O(27) = 2.81(1), and N(20)···N(23) = 2.86(1) Å for Fe2, respectively. The water O(27) is further hydrogen-bonded to an oxygen atom of a perchlorate ion O(9) with the distance of O(9)···H–O(27) = 2.94(2) Å to form a 1-D chain involving the Fe2 site and running along the *c*-axis. There are no further intermolecular hydrogen bonds less than 3.00 Å for the Fe1 site, since the corresponding distance of O(13)···H–O(28) = 3.05(3) Å is too long for a hydrogen bond. Based on the above structural parameters, we suggest that the Fe1 site is involved with the first-step spin conversion and then the Fe2 site is involved with the second-step conversion as the temperature increases.

The pressure induced spin crossover was investigated by variable pressure IR spectroscopy at 295 K and the result is shown in Figure 3.[7] The Fe–N bond distance is very sensitive to the spin state of the Fe ion and as a result the C=N bond at the Schiff-base tripodal ligand is affected by the spin state. Since the C=N stretching vibration in the IR spectrum shows an intense and sharp absorption at ca. 1600 cm^{-1}, the C=N band is a good probe to monitor the spin state. The spectrum at atmospheric pressure at 295 K shows two peaks at 1633 and 1625 cm^{-1}, which can be assigned to the C=N vibrations of high- and low-spin Fe(III) species, respectively. The observation of two C=N bands indicates the coexistence of high- and low-spin species, consistent with the result of the magnetic measurements. As the pressure increased, the peak at 1633 cm^{-1} decreased in intensity and disappeared at 1.1 GPa, while the band at 1625 cm^{-1} increased in relative intensity. The data demonstrate that a grad-
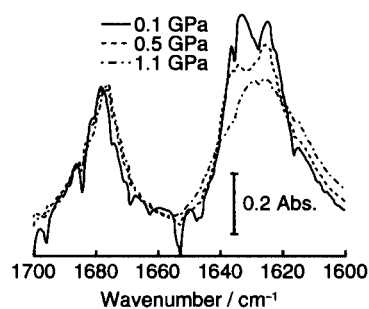
Figure 3. The pressure dependant IR spectra at 295 K.

ual spin conversion from high- to low-spin state occurs as the pressure increases.

This study revealed that the iron complex with a tripod-type ligand containing three imidazole groups can give a novel spin crossover complex. An extensive study for the family of spin crossover Fe(II), Fe(III), mixed-valence Fe(II)–Fe(III) complexes with tripodal ligands is now in progress in our laboratory.

References and Notes

1   a) O. Kahn, "Molecular Magnetism," VCH Publishers, Inc., Weinheim, (1993). b) S. Decurtins, P. Gütlich, C. P. Köhler, H. Spiering, and A. Hauser, *Chem. Phys. Lett.*, **105**, 1 (1984). c) P. Gütlich, A. Hauser, and H. Spiering, *Angew. Chem., Int. Ed. Engl.*, **33**, 2024 (1994).
2   O. Kahn and J. C. Martinez, *Science*, **279**, 44 (1998).
3   a) J-F. Létard, J. A. Real, N. Moliner, A. B. Gaspar, L. Capes, O. Cador, and O. Kahn, *J. Am. Chem. Soc.*, **121**, 10630 (1999). b) P. Gütlich, Y. Garcia, and H. A. Goodwin, *Chem. Soc. Rev.*, **29**, 419 (2000). c) S. Hayami, Z. Gu, M. Shiro, Y. Einaga, A. Fujishima, and O. Sato, *J. Am. Chem. Soc.*, **122**, 7126 (2000).
4   Synthesis of [Fe(H$_3$L)](ClO$_4$)$_3$·(4-fim)·H$_2$O: Tris(2-aminoethyl)amine (0.731 g, 5 mmol) was added to a solution of 4-formylimidazole (1.441 g, 15 mmol) in 30 mL of water, and the mixture was stirred at 60 °C for 30 min. With cooling in an ice bath, a solution of FeCl$_3$ (0.831 g, 5 mmol) in 10 mL of water was added to the mixture. After stirring for 30 min with cooling, a solution of NaClO$_4$ (1.837 g, 15 mmol) in 10 mL of water was added. The mixed solution was filtered and the filtrate was allowed to stand overnight in a refrigerator. The dark red crystals were collected by suction filtration, washed with methanol, then a minimum volume of water, and dried in vacuo. Yield: 0.407 g (10%). Anal. Calcd for [Fe(H$_3$L)](ClO$_4$)$_3$·(4-fim)·H$_2$O, C$_{22}$H$_{30}$N$_{12}$O$_{14}$Cl$_3$Fe: C, 31.13; H, 3.56; N, 19.80%. Found: C, 31.19; H, 3.54; N, 19.88%. IR(KBr): $\nu_{C=O}$(4-formylimidazole), 1678 cm^{-1}, $\nu_{C=N}$(imine), 1633, 1625 cm^{-1}; ν_{Cl-O}(ClO$_4^-$) 1112, 1086 cm^{-1}. Λ_M: 301 S mol^{-1} cm^2 in water.
5   Magnetic susceptibilities were measured with an MPMS5 SQUID susceptometer (Quantum Design, Inc.) in the 2–300 K temperature range under an external magnetic field of 1 T. The calibrations were done with palladium. Corrections for diamagnetism were applied using Pascal's constants
6   Crystal data: Data were collected over the 2θ range 2.5–50° on a Rigaku AFC-7R X-ray diffractometer with Mo Kα radiation at 293.2 K. C$_{22}$H$_{30}$N$_{12}$O$_{14}$Cl$_3$Fe, fw = 848.76. Dark red prismatic. Crystal dimensions = 0.5 × 0.3 × 0.2 mm, monoclinic, space group = *Cc* (no. 9), *a* = 38.593(3), *b* = 12.709(3), *c* = 14.175(2) Å, *β* = 95.51(1)°, *V* = 6920(2) Å^3, *Z* = 8, *F*(000) = 3480, λ = 0.71069 Å, μ(Mo Kα) = 7.489 cm^{-1}, reflections collected 6193, independent reflections 6090, [*R*(int) = 0.0114], T_{min} = 0.742, T_{max} = 0.797, *R* = 0.042, R_w = 0.025, goodness of fit = 2.920, [4659 *I* > 2.00σ(*I*)], Flack parameter = −0.026(2), (Δ/ρ)$_{max}$ = 0.31 Å^3, (Δ/ρ)$_{min}$ = −0.31 Å^3, ($R = \Sigma || F_O | - | F_C || / \Sigma | F_O |$ and $R_w = [\Sigma w(| F_O | - | F_C |)^2 / \Sigma w| F_O |^2]^{1/2}$).
7   High hydrostatic pressure was generated using a diamond anvil cell of the Basset type. A stainless steel foil of 0.03 mm in thickness was used as a gasket with an aperture of 0.6 mm in diameter. Liquid paraffin was used as a pressure medium. Pressure was determined by a ruby-fluorescence method. The homogeneity of pressure in the diamond anvil cell was confirmed by the observation of the peak width of the ruby fluorescence.