Steep Spin-crossover and LIESST Effect of a New Fe(II) Complex with a Tridentate Ligand Derived from 2-Phenyl-4-formylimidazole and *N*-Methylethylenediamine

Haruna Torigoe, Hiroaki Hagiwara, Shinobu Arata, Masahiro Yamada, and Naohide Matsumoto*
Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555

(Received April 22, 2005; CL-050550)

A novel Fe^{II} spin-crossover (SC) complex, $[Fe^{II}(HL)_2](ClO_4)_2$, has been synthesized, where HL denotes tridentate N_3 ligand *N*-methyl[2-[[(2-phenylimidazol-4-yl)methylidene]amino]ethyl]amine). The Fe^{II} complex showed a steep SC at $T_{1/2} = 175$ K without frozen-in effect and hysteresis. The crystal structures at the high-spin (HS) and low-spin (LS) states were determined. Though there is no intermolecular interaction and no frozen-in effect, LIESST (light-induced excited spin state trapping) and reverse-LIESST effects were observed.

The spin crossover (SC) between the LS and HS states is induced by temperature, pressure, or light irradiation.[1] SC complex can be applied to information storage, molecular switches and visual displays, if the SC complex assumed the hysteresis and LIESST (light-induced excited spin state trapping) effect.[2] Previously, we have reported a new family of SC complexes with tripod ligands involving three imidazole groups.[3] Some of the complexes, $[Fe^{II}H_3L^R][Fe^{II}L^R]X$ and $[Fe^{II}H_3L^R][Fe^{III}L^R]X_2$, showed interesting physical properties such as steep, multi-steps SC behaviors, hysteresis, chiral aggregation, and mixed-valence states. In this study, we studied a Fe^{II} complex with the tridentate ligand involving one imidazole group, where the tridentate ligand (HL) is derived by the 1:1 condensation reaction of 2-phenyl-4-formylimidazole and *N*-methylethylenediamine. We report here the steep SC behavior, the crystal structures at the HS and LS states, and the LIESST and reverse-LIESST effects.

Complex $[Fe^{II}(HL)_2](ClO_4)_2$ was obtained as orange rhombic crystals.[4] Orange crystals thus obtained are stable in open atmosphere. The complex showed a thermochromism from orange at 300 K to red at liquid nitrogen temperature.

The magnetic susceptibilities of the polycrystalline sample were measured in the temperature range of 5–300 K at a sweep mode rate of $1\,K\,min^{-1}$. The sample was quickly cooled to 5 K from room temperature and the magnetic susceptibility was measured while raising the temperature from 5 to 300 K. Subsequently, the magnetic susceptibility was measured while lowering the temperature from 300 to 5 K. The $\chi_M T$ vs T plots (χ_M is the molar magnetic susceptibility and T the absolute temperature) are shown in Figure 1. The magnetic behaviors during the warming and cooling modes are very similar, showing no frozen-in effect and no hysteresis. The $\chi_M T$ vs T plots showed a steep SC behavior at $T_{1/2} = 175$ K, whose value was obtained by the first derivative of $\chi_M T$. The $\chi_M T$ value is constant in the 300–230 K temperature range at ca. $3.5\,cm^3\,K\,mol^{-1}$, which indicates that Fe^{II} is in the HS state ($S = 2$). The value of $0.3\,cm^3\,K\,mol^{-1}$ in the bottom plateau region of 130–5 K is close to that expected for Fe^{II} LS state ($S = 0$).

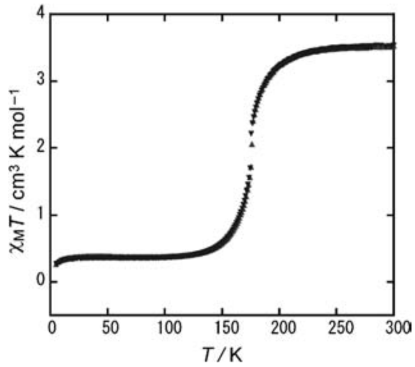

Figure 1. Magnetic behavior of $[Fe^{II}(HL)_2](ClO_4)_2$ in the form of $\chi_M T$ vs T plots in the warming (▲) and cooling (▼) modes.

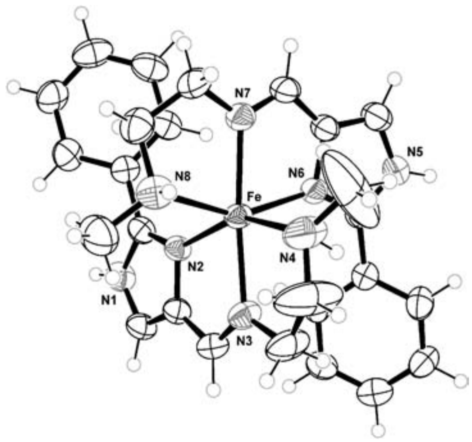

Figure 2. Molecular structure of $[Fe^{II}(HL)_2](ClO_4)_2$ at 230 K.

In order to study the molecular structures at the LS and HS states, the X-ray crystal structure analyses were carried out at 130 and 230 K.[5] The crystallographic data at the two temperatures are similar to each other and no crystallographic phase transition occurs during the LS to HS transition. Figure 2 shows the molecular structure of the complex with the atom-numbering scheme at 230 K. The Fe^{II} ion is in an octahedral coordination environment and coordinated by N_6 donor atoms of two tridentate Schiff-base ligands. During the HS at 230 K to LS at 130 K transition, the cell volume changed from $3124\,Å^3$ at 230 K to $3050\,Å^3$ at 130 K, the volume reduction being 2.4%. The unit cell volume reduction of 2.4% upon the HS → LS transition is smaller than the reported values of the similar $Fe^{II}N_6$ SC complexes (ca. 5%). On the basis of the Fe–N bond distances and N–Fe–N bond angles, the spin state can be identified. The Fe–N bond distances at 230 K are distributed in the range of 2.112(3)–2.250(4) Å, whose values are the typical distances expected for the HS Fe^{II} complex, while the Fe–N bond distances at 130 K are distributed in the range of 1.919(4)–2.057(4) Å, whose values are the typical distances expected for the LS Fe^{II} complex. The difference between the average Fe–N bond lengths of 2.191 Å (HS) and 2.000 Å (LS) is 0.191 Å, whose value is comparable with the HS–LS difference of ca. 0.2 Å reported for the Fe^{II} SC complexes with the same N_6 donor atoms. The N–Fe–N bond angles also indicate the spin state of the Fe^{II} ion, since the angles at 130 K are closer to a regular octahedron than that at 230 K (for example, N(2)–Fe(1)–N(3), 75.4(1)° at 230 K, and N(2)–Fe(2)–N(3), 80.3(1)° at 130 K).

Each perchlorate anion is hydrogen-bonded to the imidazole NH groups with the distances of N(1)···O(5) = 2.895 Å and N(5)···O(3) = 2.876 Å at 230 K, N(1)···O(6) = 2.819 Å and N(5)···O(2) = 2.822 Å at 130 K. As the result, two imidazole groups per one molecule are blocked by the perchlorate ions and further molecular interaction is prohibited. A careful investigation on the crystal structure demonstrated that there is no intermolecular interaction and no extended structure. The complex can be described as an isolated molecule structurally.

The sample was placed at the edge of the optical fiber and light with the maximum wavenumber of 600 nm was irradiated, where light passed through an interference filter with an 80 nm FWHM and the power of the light is 2 mW cm^{-2}. The light irradiations for 380 min at 5 K afforded an increase of the $\chi_M T$ value to reach the saturated value. The increase in the $\chi_M T$ value is attributed to the spin transition from the LS to HS state due to the light irradiation, that is, the so-called LIESST effect.[2] As shown in Figure 3, the photoexcitation from LS to HS is almost complete. After the light was switched off, the thermal relaxation was studied. Upon elevating the temperature from 5 K, the $\chi_M T$ value increases because of the zero field splitting effect of HS Fe^{II} and reaches the maximum value of ca. 3.3 cm^3 K mol^{-1} at 35 K and then abruptly decreases around 50 K. The maximum value of ca. 3.3 cm^3 K mol^{-1} at 35 K suggests that the Fe^{II} site completely converts from the LS to HS state owing to the LIESST effect. Figure 4 shows that orange light (λ = 600 nm) and red laser light (λ = 806 nm) irradiation is effective for the LIESST and reverse-LIESST effects, respectively. After the sample was irradiated with the 600 nm light at 5 K for 330 min, where the saturated $\chi_M T$ value was ca. 2.0 cm^3 K mol^{-1}, the light irradiation was then turned off, and the saturated $\chi_M T$ value was retained at least for 130 min. The sample was subsequently irradiated with the red laser light for 350 min, inducing a $\chi_M T$ decrease to 1.2 cm^3 K mol^{-1}, because of partial HS to LS Fe^{II} spin transition, the so-called reverse-LIESST. LIESST and reverse-LIESST effects were repeatedly observed by irradiation of 600 and 806 nm lights, as shown in Figure 4.

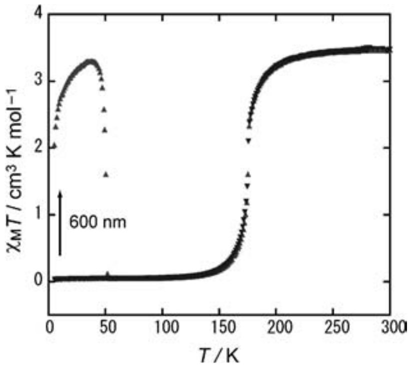

Figure 3. After the light irradiation (λ_{max} = 600 nm, 380 min) at 5 K was switched off, the thermal relaxation was recorded.

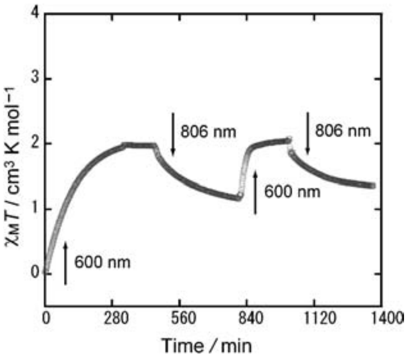

Figure 4. Time dependence of $\chi_M T$ during light irradiation of 600 nm and 806 nm, showing the LIESST effect and the partial reverse-LIESST effect.

In summary, a novel SC complex with a tridentate ligand involving imidazole group has been reported. The complex showed a steep SC, LIESST, and reverse-LIESST effects. It is easy to modify the chemical structure of the present complex so that the SC complex with more valuable properties such as wide hysteresis and high $T_{1/2}$ can be generated.

This work was supported by a Grant-in-Aid for Science Research (No. 16205010) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and Notes

1 a) For a general overview, "Topics in Current Chemistry," ed. by P. Gutlich and H. A. Goodwin (2004), Vol. 233.

2 a) A. Hauser, *Coord. Chem. Rev.*, **111**, 275 (1991). b) O. Kahn and J. C. Martinez, *Science*, **279**, 44 (1998).

3 a) Y. Sunatsuki, Y. Ikuta, N. Matsumoto, M. Kojima, S. Iijima, S. Hayami, Y. Maeda, S. Kaizaki, F. Dahan, and J. P. Tuchagues, *Angew. Chem., Int. Ed.*, **42**, 1514 (2003). b) Y. Sunatsuki, H. Ohta, M. Kojima, Y. Ikuta, Y. Goto, N. Matsumoto, S. Iijima, H. Akashi, S. Kaizaki, F. Dahan, and J.-P. Tuchagues, *Inorg. Chem.*, **43**, 4154 (2004). c) M. Yamada, M. Ooiidemizu, Y. Ikuta, S. Osa, N. Matsumoto, S. Lijima, M. Kojima, F. Dahan, and J.-P. Tuchagues, *Inorg. Chem.*, **42**, 8406 (2003).

4 The synthesis of Fe^{II} complex was carried out under nitrogen atmosphere. Tridentate ligand (HL = *N*-methyl[2-[[(2-phenylimidazol-4-yl]-methylidene]amino)ethyl]amine) was prepared by mixing 2-phenyl-4-formylimidazole (0.344 g, 2 mmol) and *N*-methylethylenediamine (0.154 g, 2 mmol) in 20 mL of methanol. Complex $[Fe^{II}(HL)_2](ClO_4)_2$ was obtained as orange rhombic crystals by standing the mixed solution of the ligand solution and $Fe^{II}(ClO_4)_2 \cdot 6H_2O$ (0.372 g, 1 mmol) in 25 mL of methanol at ambient temperature. Anal. Calcd for $C_{26}H_{32}N_8Cl_2O_8Fe$: C, 43.90; H, 4.53; N, 15.75%. Found: C, 43.52; H, 4.30; N, 15.61%.

5 X-ray crystallographic data for $[Fe^{II}(HL)_2](ClO_4)_2$ at 230 K: formula $FeC_{26}H_{32}N_8Cl_2O_8$, fw 711.34, monoclinic, space group $P2_1/n$ (No. 14), a = 12.498(3), b = 19.203(5), c = 13.054(3) Å, β = 94.15(1)°, V = 3124(1) Å^3, Z = 4, D_{calcd} = 1.512 g cm^{-3}, μ(Mo Kα) = 7.137 cm^{-1}, 7119 unique (R_{int} = 0.036), R = 0.062, Rw = 0.177, GOF = 1.004. X-ray crystallographic data at 130 K, monoclinic, space group $P2_1/n$ (No. 14), a = 12.396(5), b = 19.372(7), c = 12.711(6) Å, β = 92.20(2)°, V = 3050(2) Å^3, Z = 4, D_{calcd} = 1.549 g cm^{-3}, μ(Mo Kα) = 7.312 cm^{-1}, 6957 unique (R_{int} = 0.051), R = 0.068, Rw = 0.185, GOF = 1.000.

Published on the web (Advance View) June 4, 2005; DOI 10.1246/cl.2005.956