Abrupt Spin Transitions and LIESST Effects Observed in Fe^{II} Spin-crossover Complexes with Extended π-Conjugated Schiff-base Ligands Having N_4O_2 Donor Sets

Takayoshi Kuroda-Sowa,*[1] Zhong Yu,[1] Yuka Senzaki,[1] Kunihisa Sugimoto,[2,†] Masahiko Maekawa,[1]
Megumu Munakata,[1] Shinya Hayami,[3,††] and Yonezo Maeda[3]
[1]*Department of Chemistry, Faculty of Science and Engineering, Kinki University, Higashi-Osaka, Osaka 577-8502*
[2]*Rigaku Corporation, 3-9-12 Matsubara-cho, Akishima, Tokyo 196-8666*
[3]*Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Fukuoka 812-8581*

(Received September 5, 2008; CL-080846; E-mail: kuroda@chem.kindai.ac.jp)

Novel Fe^{II} complexes with N_4O_2 donor sets having extended π-conjugated aromatic rings, $[Fe(qnal)_2]{\cdot}CH_2Cl_2$ and $[Fe(qnal)_2]$, show abrupt spin transitions at 220 and 265 K, respectively. Both complexes show LIESST effects below 80 K.

A spin-crossover phenomenon together with a light-induced excited spin state trapping (LIESST) effect is one of the most fascinating research topics in coordination chemistry.[1] The most extensively studied spin-crossover system is the Fe^{II} d^6 system owing to the largest change of the spin-value S from 0 in the low-spin (LS) state to 2 in the high-spin (HS) state and to the availability of Mössbauer spectra to detect the electronic state of the Fe^{II} ion. Among them, those exhibiting abrupt spin transitions[2,3] especially attract considerable attention because an abruptness of the transition together with a wide hysteresis are both important factors to utilize them as memory devices in future applications. Recent developments indicate that weak interactions such as hydrogen bonding[2] and/or π–π interaction[3] between neighboring molecules are key factors to show abrupt spin transitions. In order to obtain novel spin-crossover systems with more pronounced abrupt spin transition and wider hysteresis, we have introduced an extended π-conjugated ligand qnal (Hqnal = N-(8′-quinolyl)-2-hydroxy-1-naphthaldimine) to form a Fe^{II} complex. Here we report abrupt spin transitions together with LIESST effects observed for a novel Fe^{II} complex $[Fe(qnal)_2]{\cdot}CH_2Cl_2$ ($\mathbf{1}{\cdot}CH_2Cl_2$) and its desolvated analogue.

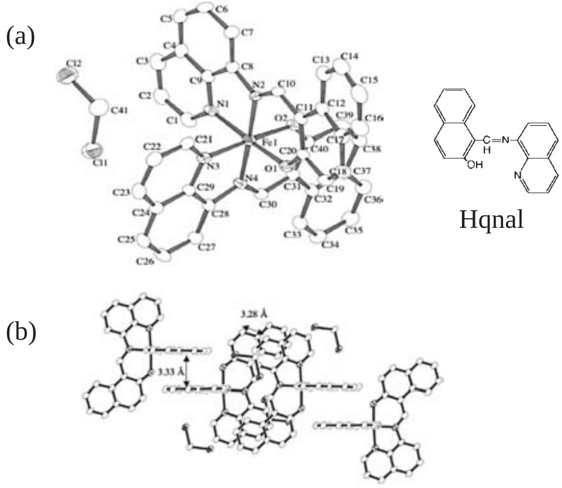

Figure 1. (a) ORTEP drawing of $[Fe(qnal)_2]{\cdot}CH_2Cl_2$ and (b) a side view of the 1-d chain connected through π–π interactions between neighboring molecules in $[Fe(qnal)_2]{\cdot}CH_2Cl_2$. Hydrogen atoms are omitted for clarity.

The iron(II) complex $\mathbf{1}{\cdot}CH_2Cl_2$ was synthesized under argon atmosphere by mixing a methanol solution of Hqnal (59.6 mg, 0.2 mmol) and a dichloromethane solution of iron(II) tetrafluoroborate (33.8 mg, 0.1 mmol). Black, needle-shape crystals suitable for X-ray analysis were obtained by slow diffusion of two solutions in a glass tube.[4] The structure of $\mathbf{1}{\cdot}CH_2Cl_2$ was determined both at 123 and 293 K, which correspond to the LS and HS states, respectively.[5] An ORTEP drawing of $\mathbf{1}{\cdot}CH_2Cl_2$ is shown in Figure 1a with atom numbering scheme. Two qnal ligands show almost planar structures: dihedral angles between quinoline and naphthalene moieties are 11.9° (qnal-A) and 1.7° (qnal-B) at 123 K. Each qnal coordinates to a Fe^{II} ion through its NNO donor set in a meridional fashion. Average bond lengths around the Fe^{II} ion at 123 K are 1.94(1) and 1.942(4) Å for four Fe–N bonds and for two Fe–O bonds, respectively. Those at 293 K are 2.16(3) and 2.016(4) Å, respectively. The increases of 0.22 Å for the average Fe–N bond and of 0.074 Å for the average Fe–O bond are comparable to those reported for Fe^{II} spin-crossover systems in FeN_6 or FeN_4O_2 coordination environments.[1,6] Since a planer qnal ligand has a rather stiff geometry, elongations in Fe–N bond lengths cause a severe deformation of Fe^{II} coordination geometry: the angle ∠N1–Fe–O1 of 161.1° at 293 K indicates a bent structure compared to that at 123 K (176.0°). Both the elongation and the deformation reduce the t_{2g}–e_g energy separation in a simplified electronic structure, giving a HS state as a ground state. As shown in Figure 1b, there are rich π–π interactions between quinoline and naphthalene moieties of neighboring molecules. A detail inspection of the connectivity of the π–π interaction indicates the complex forms one dimensional chain structure with ···[A:Fe:B][B:Fe:A][A:Fe:B]···, where [A:Fe:B] represents a $[Fe(qnal)_2]$ complex. The shortest C···C distances are 3.280 Å for $A_q{\cdots}A_n$ and 3.328 Å for $B_q{\cdots}B_n$, where suffixes q and n represent quinoline and naphthalene moieties, respectively. The small difference in these distances indicates that the system can be regarded as a quasi one-dimensional system. The connectivity of π–π interaction together with the molecular packing are somewhat resembled to those of $[Fe^{III}(qsal)_2]NCE$ (E = S and Se),[7] where qsal is anion of N-(8′-quinolyl)-2-hydroxy-1-salicylaldimine. The χ_MT–T plot of $\mathbf{1}{\cdot}CH_2Cl_2$ is shown in Figure 2a. At low temperatures below 214 K, $\mathbf{1}{\cdot}CH_2Cl_2$ is diamagnetic indicating a LS ground state. With increasing temperature, the χ_MT value increased suddenly at 217 K and reached $3.73\,cm^3\,K\,mol^{-1}$ at 222 K, indicating a spin transition to a HS state. The transition occurred within a narrow temperature range of 5 K. When temperature was decreased,

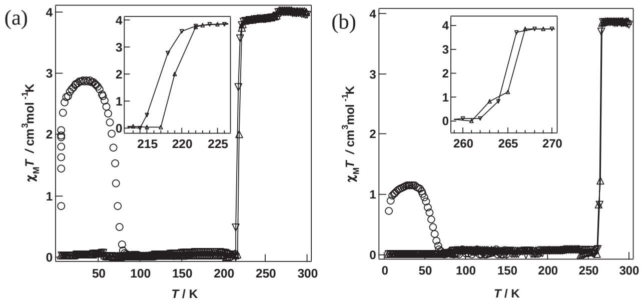

Figure 2. $\chi_M T$–T plots of [Fe(qnal)$_2$]•CH$_2$Cl$_2$ (a) and [Fe(qnal)$_2$] (b) with increasing (△) and decreasing (▽) temperature at 2 K/min. Those after photoillumination at 5 K (LIESST) are indicated by open circles (○). Insets show the enlargements around each spin-transition temperature.

the $\chi_M T$ value decreased from 3.78 cm^3 K mol^{-1} at 222 K to 0 at 214 K. The critical temperatures $T_{1/2}\uparrow$ and $T_{1/2}\downarrow$, which are defined as temperatures at which a half of the spin transition has completed for warming and cooling processes, are 219 and 217 K, respectively. It should be noted that, on the contrary to our expectation, the system showed a very narrow hysteresis loop in spite of an abrupt spin transition.

Mössbauer spectra of **1**•CH$_2$Cl$_2$ observed at 205 K[10] showed doublet peaks split with $\Delta E_Q = 1.20$ mm s^{-1} at the isomer shift (σ) of 0.36 mm s^{-1}, indicating a LS Fe^{II} center. A fairly large ΔE_Q for a LS Fe^{II} center is ascribed to the N$_4$O$_2$ coordination environment.[8] These features converted at 250 K to $\Delta E_Q =$ 2.47 and $\sigma = 0.93$ mm s^{-1}, which are typical values for a HS Fe^{II} center.

A small increase of the $\chi_M T$ at around 265 K in Figure 2a suggested the presence of a small amount of another spin-crossover phase such as **1** without crystalline solvent. To check the possibility thermogravimetric analysis was conducted. A gradual decrease of sample mass occurred at ca. 120 °C and a total decrease of ca. 10.3% was observed at 190 °C, which corresponds to a loss of CH$_2$Cl$_2$ from **1**•CH$_2$Cl$_2$ (11.5%). The $\chi_M T$–T plot of **1** without crystalline solvent is shown in Figure 2b, which exhibits a sharp spin transition at around 265 K. The increase of $T_{1/2}$ about 47 K by removing crystalline solvent indicates a perturbation of a molecular packing affects the $T_{1/2}$ drastically. The attempts to get the crystal structure of **1** without crystalline solvent were unsuccessful.

When a microcrystalline sample of **1**•CH$_2$Cl$_2$ was illuminated at 5 K with ca. 550-nm light (a Hg–Xe lamp with green and blue filtered, 1.5 mW/cm^2) introduced into the SQUID sample chamber through an optical fiber, an increase of the $\chi_M T$ value to 2.2 cm^3 K mol^{-1} was observed. After illumination was turned off, the magnetization was measured with increasing temperature at 2 K/min. As shown in Figure 2a with open circles (○), the $\chi_M T$ value showed a maximum of 3 cm^3 K mol^{-1} at 30 K and decreased gradually to 2.7 cm^3 K mol^{-1} at 50 K then dropped sharply to 0 at around 80 K. The characteristic LIESST temperature T_{LIESST}[9] estimated from the maximum variation of the $\chi_M T$–T plot after LIESST is about 71 K. A similar behavior was also observed for the complex **1** without crystalline solvent as shown in Figure 2b with open circles, although the HS fraction at 30 K is almost half of the former. The characteristic LIESST temperature T_{LIESST} for **1** is about 57 K.

In conclusion, two Fe^{II} spin-crossover systems having N$_4$O$_2$ donor sets, [Fe(qnal)$_2$]•CH$_2$Cl$_2$ and desolvated [Fe(qnal)$_2$], show abrupt spin transitions at around 220 and 265 K respectively. The abruptness of transitions is caused by rich π–π interactions through qnal ligands. Both spin-crossover systems show LIESST effects below 80 K.

References and Notes

† Present address: Japan Synchrotron Radiation Research Institute, Kouto, Mikazuki, Sayo-gun, Hyogo 679-5198

†† Present address: Department of Chemistry, Graduate School of Science, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739-8526

1 a) H. A. Goodwin, *Coord. Chem. Rev.* **1976**, *18*, 293. b) P. Gütlich, A. Hauser, *Coord. Chem. Rev.* **1990**, *97*, 1. c) P. Gütlich, A. Hauser, H. Spiering, *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2024. d) J. A. Real, A. B. Gaspar, M. C. Muñoz, *Dalton Trans.* **2005**, 2062, and references cited therein.

2 V. Niel, A. L. Thompson, M. C. Muñoz, A. Galet, A. E. Goeta, J. A. Real, *Angew. Chem., Int. Ed.* **2003**, *42*, 3760.

3 a) J. A. Real, B. Gallois, T. Granier, F. Suez-Panamá, J. Zarembowitch, *Inorg. Chem.* **1992**, *31*, 4972. b) J. A. Real, M. C. Muñoz, E. Andrés, T. Granier, B. Gallois, *Inorg. Chem.* **1994**, *33*, 3587. c) J.-F. Létard, P. Guionneau, L. Rabardel, J. A. K. Howard, A. E. Goeta, D. Chasseau, O. Kahn, *Inorg. Chem.* **1998**, *37*, 4432.

4 Anal. Calcd for C$_{41}$H$_{28}$Cl$_2$FeN$_4$O$_2$ **1**•CH$_2$Cl$_2$: C, 66.96; H, 3.84; N, 7.62%. Found: C, 66.14; H, 4.22; N, 7.70%. Anal. Calcd for C$_{40}$H$_{26}$FeN$_4$O$_2$ **1**: C, 73.85; H, 4.03; N, 8.61%. Found: C, 72.55; H, 4.56; N, 9.28%.

5 Crystal data for **1**•CH$_2$Cl$_2$ at 123.1 K: C$_{41}$H$_{28}$Cl$_2$FeN$_4$O$_2$, $M_r = 735.46$, Triclinic, space group $P\bar{1}$ (no. 2), $a = 12.201(6)$, $b = 12.550(6)$, $c = 12.985(7)$ Å, $\alpha = 98.064(3)°$, $\beta = 116.469(8)°$, $\gamma = 110.004(7)°$, $V = 1568.1(14)$ Å^3, $Z = 2$, $D_{\text{calcd}} = 1.558$ g cm^{-3}, μ (Mo Kα) $= 0.701$ cm^{-1}. At 293.1 K: Triclinic, space group $P\bar{1}$ (no. 2), $a = 11.988(2)$, $b = 12.631(2)$, $c = 13.462(3)$ Å, $\alpha = 97.96(2)°$, $\beta = 117.36(2)°$, $\gamma = 108.30(3)°$, $V = 1619.3(9)$ Å^3, $Z = 2$, $D_{\text{calcd}} = 1.508$ g cm^{-3}, μ (Mo Kα) $= 0.676$ cm^{-1}. Data collections were performed on a RIGAKU SATURN CCD diffractometer (Mo Kα, $\lambda = 0.71073$ Å) with θ ranges of $2.1 \leqq \theta \leqq 27.1°$ at 123.1 K and $1.8 \leqq \theta \leqq 28.7°$ at 293.1 K. The structures were solved with direct methods (SHELXS-97) and refined by full-matrix least squares (SHELXL-97), giving for **1**•CH$_2$Cl$_2$ at 123.1 K a final R_1 value of 0.0700 for 452 parameters and 4213 unique reflections with $I \geqq 2\sigma(I)$ and wR_2 of 0.1940 for all 5470 reflections, and at 293.1 K a final R_1 value of 0.0730 for 452 parameters and 1588 unique reflections with $I \geqq 2\sigma(I)$ and wR_2 of 0.1830 for all 5546 reflections. CCDC 282609 & 282610. The obtuse cell choice at 293.1 K is converted from the original acute set ($a = 11.988(2)$, $b = 12.631(2)$, $c = 13.289(2)$ Å, $\alpha = 64.94(2)°$, $\beta = 64.12(2)°$, $\gamma = 71.70(2)°$) for the easy comparison to the 123.1 K data.

6 a) D. Boinnard, A. Bousseksou, A. Dworkin, J. M. Savariault, F. Varret, J.-P. Tuchagues, *Inorg. Chem.* **1994**, *33*, 271. b) L. Salmon, A. Bousseksou, B. Donnadieu, J.-P. Tuchagues, *Inorg. Chem.* **2005**, *44*, 1763.

7 S. Hayami, Z. Gu, H. Yoshiki, A. Fujishima, O. Sato, *J. Am. Chem. Soc.* **2001**, *123*, 11644.

8 B. Weber, E. Kaps, J. Weigand, C. Carbonera, J.-F. Létard, K. Achterhold, F. G. Parak, *Inorg. Chem.* **2008**, *47*, 487.

9 J.-F. Létard, P. Guionneau, O. Nguyen, J. S. Costa, S. Marcén, G. Chastanet, M. Marchivie, L. Goux-Capes, *Chem.—Eur. J.* **2005**, *11*, 4582.

10 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) November 1, 2008; doi:10.1246/cl.2008.1216