3240 *Inorg. Chem.* **2001,** *40,* 3240−3242

A Novel LIESST Iron(II) Complex Exhibiting a High Relaxation Temperature

Shinya Hayami,[†] Zhong-ze Gu,[†] Yasuaki Einaga,[‡] Yoshio Kobayasi,[§] Yumiko Ishikawa,[▽] Yasuhiro Yamada,[▽] Akira Fujishima,[‡] and Osamu Sato*,[†]

Special Research Laboratory for Optical Science,
Kanagawa Academy of Science and Technology, East 412,
3-2-1 Sakado, Takatsu-ku, Kawasaki-shi,
Kanagawa 213-0012, Japan, Department of Applied
Chemistry, The University of Tokyo, 7-3-1 Hongo,
Bunkyo-ku, Tokyo 113-8656, Japan, RIKEN Hirosawa,
Wako, Saitama 351-0198, Japan, and Department of
Chemistry, Faculty of Science, Science University of Tokyo,
Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

Received June 27, 2000

Introduction

A number of spin-crossover complexes have been studied.[1] These compounds are important in the development of electronic devices such as molecular switches. Seventeen years ago Decurtins et al. observed a light-induced low-spin (LS) → high-spin (HS) transition, during which the molecules can be quantitatively trapped in the excited HS state at sufficiently low temperatures.[2] This phenomenon is called light-induced excited spin state trapping (LIESST). The discovery of this LIESST effect suggested that the spin-crossover compounds could be used as optical switches. In the meantime, a number of iron compounds with long-lived light-induced metastable HS states at low temperatures have been found.[2−8] However, the LIESST effect has been observed only at sufficiently low temperatures, below 80 K so far.[3−5] We directed our research toward the production of compounds which can be switched by illumination and in which the metastable HS state can be trapped at higher temperature.

The iron(II) complex we focused on is $[Fe(L)(CN)_2]\cdot H_2O$ (**1**), where L is a Schiff-base macrocyclic ligand derived from the condensation of 2,6-diacetylpyridine with 3,6-dioxaoctane-1,8-diamine. The temperature-dependent spin-crossover phenomenon, $S = 0$ (LS) ↔ $S = 2$ (HS) of the complex **1**, was extensively studied 15 years ago by König et al.[9,10] They reported that the powder samples of complex **1** exhibited unusual magnetic behavior. However, the physical properties of single crystals, and the photoinduced spin transition have not been reported yet.

Here, we synthesized the single crystal form of complex **1** and also investigated its crystal structure. Moreover, we have discovered that complex **1** exhibits LIESST effects. The relaxation temperature from the metastable HS to the original LS state is above 130 K, which is the highest temperature investigated so far.[3−5]

Experimental Section

Synthesis. The iron(II) complex $[Fe(L)(CN)_2]\cdot H_2O$ (**1**) was prepared by template synthesis, following a method described previously.[9] Violet single crystals of **1** were obtained by the diffusion method after 2 days.

X-ray Crystallography. A violet platelet crystal of **1,** having approximate dimensions of 0.2 × 0.2 × 0.05, was mounted in a glass capillary. Crystal data for $C_{17}H_{23}O_3N_5Fe$: $M = 401.25$, monoclinic, space group C_c ($Z = 4$); $a = 17.282(1)$, $b = 12.045(9)$, $c = 10.1336(8)$ Å; $\beta = 116.301(2)°$; $V = 1891.1(2)$ Å^3; $D_c = 1.409$ g cm^{-3}; μ(Mo Kα) = 8.2 cm^{-1}. All measurements were made on a Rigaku RAXIS−RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation. Data were collected at 270 K on a Rigaku Raxis-Rapid IP diffractometer. Of the 8753 reflections which were collected, 2168 were unique ($R_{int} = 0.028$), and 1870 with I > 3ó (I) were used to solve the structure with SIR92. Final R values gave $R1 = 0.038$ for I > 3ó(I), $R = 0.085$ and $R_w = 0.109$ for all data. The non-hydrogen atoms were refined anisotoropically. Hydrogen atoms were included but not refined.

Susceptibility Measurements. The magnetic susceptibilities $\chi(T)$ for compound **1** between 5 and 300 K were measured with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5S) in an external field of 0.5 T.

Mössbauer Spectroscopy. The Mössbauer spectra (isomershift vs metal iron at room temperature) were measured using a Wissel MVT-1000 Mössbauer spectrometer, with a ^{57}Co/Rh source, in the transmission mode. The measurements at low temperature were performed with a closed-cycle helium refrigerator (Iwatani Co., Ltd.).

Results and Discussion

At 270 K, the thermodynamically stable form of complex **1** is an HS state. The molecular and crystal structures of $[Fe(L)(CN)_2]\cdot H_2O$ (**1**) at 270 K are shown in Figure 1. The iron ion is in a pentagonal bipyramidal environment, with the macrocycle occupying the pentagonal girdle and two cyanide carbon atoms in the axial positions. The Fe−N bond lengths in the HS form for **1** are 2.108(3) Å (Fe(1)−N(1)), 2.127(6) Å (Fe(1)−N(2)), and 2.286(6) Å (Fe(1)−N(3)), the Fe−O bond lengths are 2.277(6) Å (Fe(1)−O(1)) and 2.405(6) Å (Fe(1)−O(2)), and the Fe−C bond lengths are equal to 2.151(9) Å (Fe(1)−C(16)) and 2.184(7) Å (Fe(1)−C(17)), respectively. The iron-cyanide bond angle C(16)−Fe(1)−C(17) is 169.5° (less than 180°). The macrocycle N_3O_2 ring, which includes the two imine bonds, is nearly planar. The maximum deviation of a contributing atom from the FeN_3O_2 least-squares plane is ca. 0.70 Å. Complex **1** contains one water molecule, which binds the $[Fe(L)(CN)_2]$ molecules by an N···O interaction (the bond lengths O(3)···N(4) and O(3•)···N(5) are 2.853(10) and 2.840(8), respectively). The

---

* To whom correspondence should be addressed.

[†] Kanagawa Academy of Science and Technology.

[‡] The University of Tokyo.

[§] RIKEN Hirosawa.

[▽] Science University of Tokyo.

(1) (a) Goodwin, H. A. *Coord. Chem. Rev.* **1976**, *18*, 293−325. (b) Gütlich, P. *Struct. Bonding (Berlin)* **1981**, *44*, 83−195. (c) Gütlich, P.; Hauser, A. *Coord. Chem. Rev.* **1990**, *97*, 1−22. (d) König, E. *Prog. Inorg. Chem.* **1987**, *35*, 527−623. (e) König, E. *Struct. Bonding (Berlin)* **1991**, *76*, 51.

(2) Decurtins, S.; Gütlich, P.; Köhler, C. P.; Spiering, H.; Hauser, A. *Chem. Phys. Lett.* **1984**, *105*, 1.

(3) Gütlich, P.; Hauser, A.; Spiering, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2024.

(4) Buchen, T.; Gütlich, P.; Goodwin, H. A. *Inorg. Chem.* **1994**, *33*, 4573.

(5) Létard, J. F.; Capes, L.; Chastanet, G.; Moliner, N.; Létard, S.; Real, J.-A.; Kahn, O. *Chem. Phys. Lett.* **1999**, *313*, 115.

(6) Létard, J. F.; Guionneau, P.; Codjovi, E.; Lavastre, O.; Bravic, G.; Chasseau, D.; Kahn, O. *J. Am. Chem. Soc.* **1997**, *119*, 10861.

(7) Hayami, S.; Gu, Z. Z.; Shiro, M.; Einaga, Y.; Fujishima, A.; Sato, O. *J. Am. Chem. Soc.* **2000**, *122*, 7126.

(8) Létard, J. F.; Nguyen, O.; Soyer, H.; Mingotaud, C.; Delhaès, P.; Kahn, O. *Inorg. Chem.* **1999**, *38*, 3020.

(9) Nelson, S. M.; McIlroy, P. D. A.; Stevenson, C. S.; König, E.; Ritter, G.; Waigel, J. *J. Chem. Soc., Dalton Trans.* **1986**, 991.

(10) König, E.; Ritter, G.; Dengler, J.; Nelson, S. M. *Inorg. Chem.* **1987**, *26*, 3582.

10.1021/ic000708e CCC: $20.00

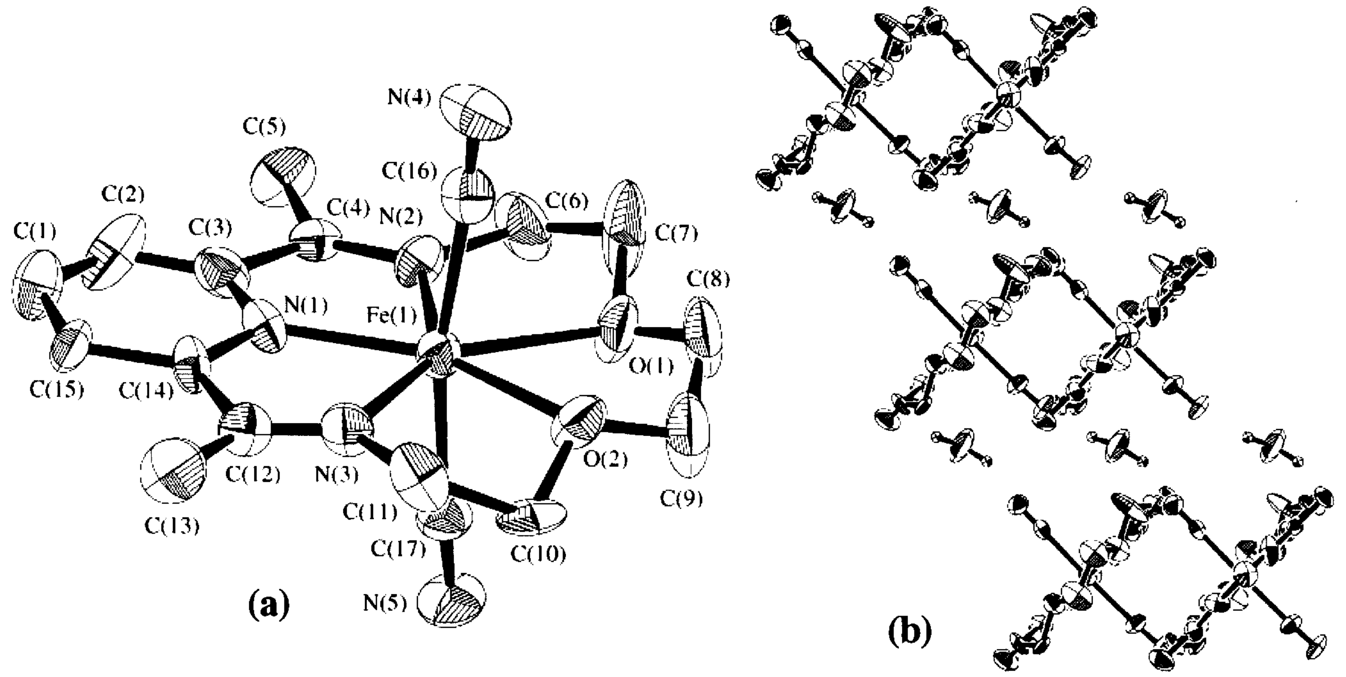

Figure 1. Molecular structures in the high-spin (270 K) states. (a) ORTEP view for complex **1** (with the exception of the hydrogen atoms and a water molecule). (b) Projection of the crystal structure of complex **1** along the *ac* plane.

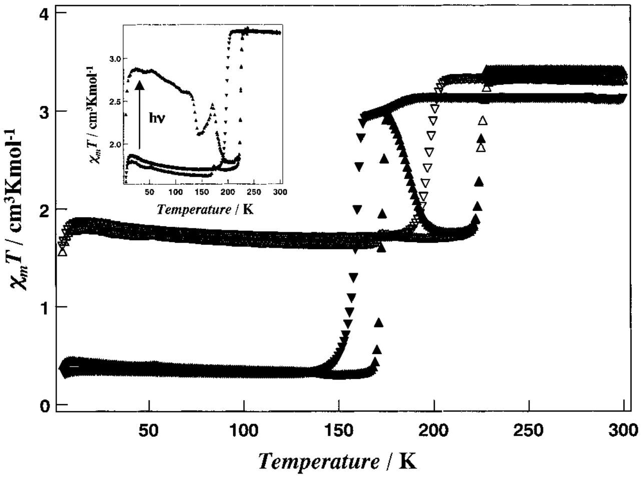

Figure 2. $\chi_m T$ versus T plots for complex **1**. (▼): Cooling mode of first cycle. (▲): Warming mode of first cycle. (▽): Cooling mode of second cycle. (△): Warming mode of second cycle. The temperature was varied at the rate of 1 K min^{-1} without temperature overshoot. The $\chi_m T$ versus T plot in the inset was recorded in the warming mode after the sample was exposed to light illumination for 1 h.

symmetric units are linked through the water molecules into infinite one-dimensional chains with the $[Fe(L)(CN)_2]$ complex lying along the *a* axis. Unfortunately, the structure of **1** in the low-spin state could not be measured because of the destruction of the single crystals.

The temperature dependence of the magnetic susceptibility for **1** was investigated in the crystals with a SQUID magnetometer (Figure 2). The product of the molar magnetic susceptibility and temperature, $\chi_m T$, at 300 K is equal to 3.3 cm^3 K mol^{-1}, which corresponds to what is expected for the HS state. On cooling, the $\chi_m T$ value slightly decreases, from 193 to 164 K (2.9 cm^3 K mol^{-1}), and then abruptly drops at around $T_{1/2}\downarrow = 159$ K. The spin transition temperature, $T_{1/2}$, is defined as the temperature at which complexes show a population of 50% in the HS and 50% in the LS states. At 130 K, $\chi_m T$ is close to zero in the single-crystal samples. In the warming mode, $\chi_m T$ rises abruptly around $T_{1/2}\uparrow = 172$ K to 3.2 cm^3 K mol^{-1}. The thermal hysteresis of 13 K in the magnetic susceptibility was observed. On further warming, the $\chi_m T$ values decrease from 3.2 cm^3 K mol^{-1} at 176 K to 1.7 cm^3 K mol^{-1} at 207 K, and they then increase again at around $T_{1/2}\uparrow = 225$ K to 3.4 cm^3 K mol^{-1}. The magnetic properties of the second thermal cycle were consistent with those of the powder sample reported previously.[9,10] That is, they show a conventional one step transition with $T_{1/2}\uparrow = 225$ K and $T_{1/2}\downarrow = 198$ K, because single crystals break into powder after the spin transition. It was found that the 50% moiety remains in the high-spin state even at 100 K. Mössbauer measurements have shown that the stable form consists of HS and LS ground states in almost equal proportion. Successive thermal cycles did not modify the thermal hysteresis loop ($\Delta T = 27$ K) of the second cycle. The abrupt transition with the hysteresis loop appears only when the cooperative effect is strong enough.[5−14] It is thought that, in the present case, the cooperation mainly arises from the formation of a one-dimensional chain of complex **1** mediated by N···O interactions. Mössbauer spectra at 300 K show a wide quadrupole doublet with Q.S. = 3.09 and I.S. = 0.83 mm s^{-1}, showing a HS state. On cooling, this spectrum decreases, and a narrow quadrupole doublet with Q.S. = 1.38 and I.S. = 0.01 mm s^{-1} appears, supporting the transition from an HS to a LS state. A bluish violet to dark purple color change accompanies this transition. The ν(C−N) stretching mode at 300 K was observed at 2106 and 2103 cm^{-1}, while, after spin transition, it was observed at 2095 cm^{-1}. Furthermore, if the sample is rapidly quenched in the liquid helium temperature cavity of the SQUID equipment, wherein the sample is cooled within a few seconds, $\chi_m T$ is 3.5

---

(11) Real, J. A.; Andrés, E.; Muñoz, M. C.; Julve, M.; Granier, T.; Bousseksou, A.; Varret, F. *Science* **1995**, *268*, 265.

(12) Xie, C.-L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 6981−6988.

(13) Conti, A. J.; Xie, C.-L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1989**, *111*, 1171−1180.

(14) Hauser, A.; Adler, J.; Gütlich, P. *Chem. Phys. Lett.* **1988**, *152*, 468−472.

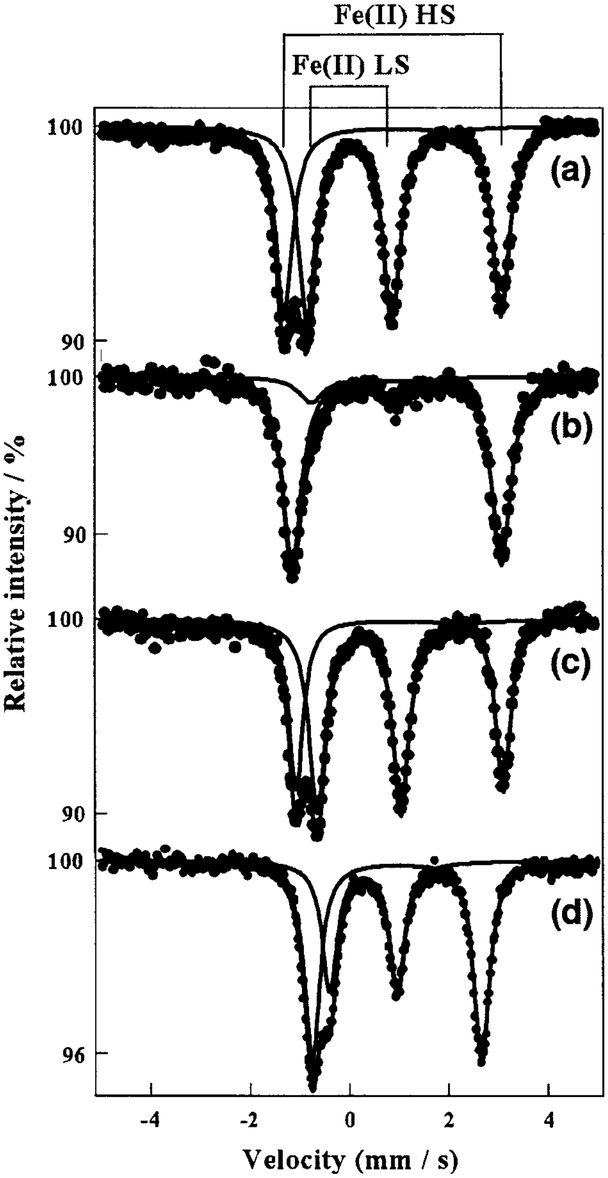

Figure 3. The ^{57}Fe Mössbauer spectra of complex **1** at 15K. (a) The original state in the second cycle, (b) after illumination at $\lambda \approx 550$ nm, (c) after thermal-induced relaxation (warmed to 250 K, then cooled back to 15 K), and (d) or after the light-induced relaxation ($T = 15$ K, $\lambda \approx 850$ nm).

cm^3 K mol^{-1}, showing that the HS state is "frozen-in", and the spin transition to the LS state is not observed even within days.[9,10,15,16] If the sample is now slowly warmed, the frozen-in spin transition HS → LS sets in at about 150 K, and $\chi_m T$ falls to 0.02 cm^3 K mol^{-1}. The metastable, "frozen-in" HS state of a spin-crossover compound is not particularly common. The bistable states, frozen-in HS and LS states, exist in the temperature range below 130 K. Therefore, the complex **1** may be suitable for LIESST experiments even at a much higher temperature, around 130 K, than that reported so far.[3-5]

A Hg−Xe lamp ($\lambda \approx 550$ nm, 1.5 mW/cm^2) was used as a light source in the investigation of illumination effects. The light passes through IR and green filters and was guided via an optical fiber into the SQUID. The sample was placed on the edge of the optical fiber. When the sample was illuminated at 5 K, an increase in the dc susceptibility was observed. The change in the magnetization persisted for many hours, even after the illumination was stopped. This suggests that the transition from the LS state to the HS state can be induced by illumination. IR spectra after illumination at 15 K show that absorption at 2095 cm^{-1} disappears and that the shifted peaks at 2113 and 2106 cm^{-1} increase in intensity. This also proves the presence of a light-induced spin transition. To quantitatively estimate the HS fraction after illumination, Mössbauer spectra were measured (Figure 3). The narrow quadruple doublets for the LS state (Q.S. = 1.38, I.S. = 0.01 mm s^{-1}) disappear after the illumination and, concomitantly, the intensity of the wide quadruple doublet for the pure HS state (Q.S. = 3.52, I.S. = 0.71 mms^{-1}) increases. That is, the LS moieties completely change to the HS state. The temperature dependence of $\chi_m T$ after irradiation is shown in the inset of Figure 2. It shows that the relaxation occurs in two steps. That is, the magnetization value decreases from 2.9 to 2.1 cm^3 K mol^{-1} at around 130 K, and then, it is completely restored to the original value (ca. 1.7 cm^3 K mol^{-1}) at around 180 K. To the best of our knowledge, this relaxation temperature, T_c(LIESST) = 130 K, is the highest reported so far.[3-5] The cycle of an increase in the magnetization by illumination and then decrease by thermal relaxation could be repeated. It should be noted that, in the interpretation of the photoprocess, heating effects should be carefully checked, because this compound exhibits a frozen-in effect.[9,10,15,16] There is a possibility that the HS state is induced via a photothermal process and is frozen-in due to the rapid quenching. However, this possibility could be ruled out in the present case, since the illumination effect depends on the excitation wavelength. That is, when the compound with a metastable (HS) state is illuminated at 15 K, by means of a Diode Laser (850 nm, 0.3 mW/cm^2), a reverse LIESST effect could be induced.

In summary, we have deduced the crystal structure of complex **1**. The structure shows that the center iron ion is coordinated with a pentadentate macrocycric and two cyanide ions. Complex **1** exhibits a LIESST effect. It was found that the T_c(LIESST) value exceeds 130 K. This temperature is the highest value reported so far for LIESST compounds.

Acknowledgment. This work was supported in part by a Joint Research Project for Regional Intensive of Kanagawa Prefecture. We thank Prof. M. Yamashita and Dr T. Ishii (Tokyo Metropolitan University) for use of the X-ray diffractometer (Rigaku IP RAPID).

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000708E

---

(15) Goodwin, H. A.; Sugiyarto, K. H. *Chem. Phys. Lett.* **1987**, *139*, 470.
(16) Ritter, G.; König, E.; Irler, W.; Goodwin, H. A. *Inorg. Chem.* **1978**, *17*, 224.