

Photo-Induced Spin Transition for an Iron(III) Pyruvic Acid Thiosemicarbazone Compound

Shinya Hayami,^{*,a} Koichiro Hashiguchi,^b Katsuya Inoue,^b and Yonezo Maeda^a^aDepartment of Chemistry, Faculty of Science, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan^bInstitute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

Received: December 11, 2003; In Final Form: February 4, 2004

An iron(III) compound [Fe(thpu)(Hthpu)] has exhibited spin transition behavior ($T_{1/2\downarrow} = 225$ K and $T_{1/2\uparrow} = 239$ K) with a thermal hysteresis loop ($\Delta T = 14$ K). When the sample has been illuminated at 5 K, an increase in the dc susceptibility was observed. This suggests that the transition from the low-spin state to the high-spin state can be induced by illumination.

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) \rightarrow high-spin (HS) transition, during which the molecules can be quantitatively trapped in the excited HS state at sufficiently low temperatures.² The phenomenon is called light-induced excited spin state trapping (LIESST), and the existence of the light-induced HS state for the iron(II) spin-crossover compounds was verified with optical, Mössbauer, and magnetic susceptibility measurements.²⁻⁷ 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(II) compounds with long-live light-induced metastable HS states at low temperatures have been found.²⁻⁷

Recently, we have succeeded in observing the LIESST effect for an iron(III) complex [Fe(pap)₂ClO₄·H₂O (Hpap = 2-hydroxyphenyl-(2-pyridyl)-methanimine) by using the newly designed ligand which enhanced cooperative behavior and strong intermolecular interactions for the first time.⁸ The planar ligand, pap, with corresponding π electrons, has a potential ability to interact with neighboring ligands by π - π interactions. In fact, the presence of a strong intermolecular interaction has been suggested from the single crystal X-ray analysis. Our purpose is to investigate the intermolecular interactions between iron(III) complexes and to stabilize long-lived metastable HS state for illuminated samples by decreasing the rate of tunneling. However, the LIESST effect for iron(III) compounds has been observed only in the compounds with π - π intermolecular interaction so far.^{8,9} We directed toward to produce the compounds, which can be switched by illumination and the metastable HS state can be trapped by introducing hydrogen bonding.

The iron(III) complex we focused on [Fe(thpu)(Hthpu)] (**1**), where H₂thpu is a tridentate Schiff-base derived from the condensation of pyruvic acid with thiosemicarbazide. The temperature dependent spin-crossover phenomenon, $S = 1/2$ (LS state) \leftrightarrow $S = 5/2$ (HS state) of the molecular complex, [Fe(thpu)(Hthpu)] (**1**) has been extensively studied by Hendrickson et al. (Figure 1).¹⁰ The compound **1** was prepared by the method described previously (Figure 2).¹¹ The thpu²⁻ (thiol form) and Hthpu⁻ (thione form) ligand is coordinated to a metal ion. Both ligands are obtained by sequentially deprotonating neutral pyruvic acid thiosemicarbazide. Unfortunately,

no single crystals of **1** were obtained. The chromium(III) compound [Cr(thpu)(Hthpu)]·H₂O was synthesized by Ablov et al.¹² and the crystal structure of the compound was determined by Hendrickson et al.¹⁰ The crystallographic study revealed the structural differences between the two ligands thpu²⁻ and Hthpu⁻. The singly deprotonated Hthpu⁻ ligand possesses a hydrogen atom bound to the nitrogen atom (=N-NH-), whereas there is no hydrogen atom at the nitrogen position of the doubly deprotonated thpu²⁻ ligand (=N-N=). It has been inferred that the crystal structure of the compound **1**

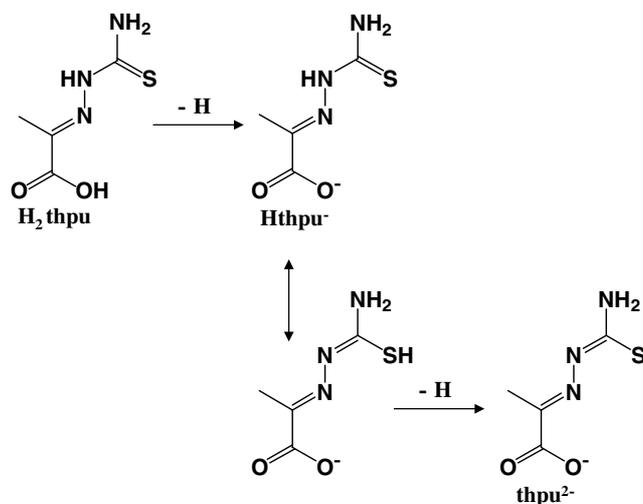


Figure 1. Derivatives after deprotonations of the H₂thpu ligand.

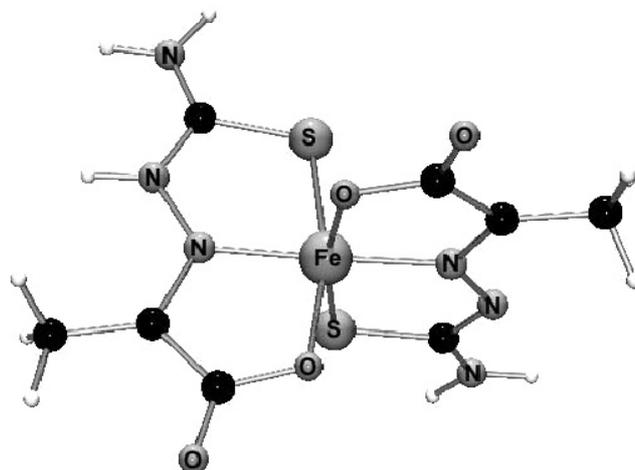


Figure 2. A proposed structure for [Fe(thpu)(Hthpu)] (**1**).

*Corresponding author. E-mail: hayasce@mbox.nc.kyushu-u.ac.jp. FAX: +81-92-642-2607.

is similar to that of chromium(III) compound by using X-ray powder diffraction patterns and IR spectra by Hendrickson et al.¹⁰ It is quite likely, thus, that the spin transition for **1** is due to the cooperative aspect of iron(III) complexes through intermolecular hydrogen bonds.

At room temperature, the thermodynamically stable form of the compound **1** is a high-spin state. Magnetic properties show that the value of $\chi_m T$ for **1** is equal to $3.69 \text{ cm}^3 \text{ K mol}^{-1}$ at room temperature, which corresponds to what is expected for HS state in iron(III) compounds (Figure 3). On cooling, the value of $\chi_m T$ drops abruptly around $T_{1/2\downarrow} = 225 \text{ K}$. The $\chi_m T$ value at 200 K is equal to $0.55 \text{ cm}^3 \text{ K mol}^{-1}$, corresponding to the LS state. In the warming mode, an abrupt variation of $\chi_m T$ is observed around $T_{1/2\uparrow} = 239 \text{ K}$. Fairly abrupt transitions with a hysteresis loop (ca. 14 K) show the presence of the strong cooperative interaction such as magnetic behavior reported by Hendrickson et al.¹⁰

Furthermore, Mössbauer spectra for **1** were measured at 80 K, 241 K and 293 K, and are shown in Figure 4. Mössbauer spectra at 80 K show a wide quadrupole doublet with quadrupole splitting $Q.S. = 3.09$ and isomer shift $I.S.$ (relative to α -iron foil at room temperature) = 0.28 mm s^{-1} , showing a LS state for iron(III) compounds. At 241 K this absorption decreases and a narrow quadrupole doublet with $Q.S. = 0.81$ and $I.S. = 0.47 \text{ mm s}^{-1}$ appears, supporting the transition from LS to a HS state at half ratio. A doublet with $Q.S. = 0.65$ and $I.S. = 0.49 \text{ mm s}^{-1}$ (line half-width $\Gamma_{1/2} = 0.35$ and 0.34 mm s^{-1}) corresponding to the HS state of iron(III) compounds was observed at 293 K. It is noticed that line half-widths $\Gamma_{1/2} \approx 0.35 \text{ mm s}^{-1}$ for **1** are such small. The iron(III) centers in the HS, if they are well isolated in molecular solids, can exhibit line half-widths greater than 1 mm s^{-1} .^{10, 13} Wignall has reported that short paramagnetic relaxation times and narrow Mössbauer line widths were observed for Fe...Fe distances of $6 - 7 \text{ \AA}$.¹³ Hendrickson et al. have been revealed by single crystal structure analysis that the Cr...Cr distances in the chromium(III) compound $[\text{Cr}(\text{thpu})(\text{Hthpu})] \cdot \text{H}_2\text{O}$ are probably quite short ($< 7 \text{ \AA}$).¹⁰ It may be thought that there is the strong intermolecular interaction in the compound **1** because the ligands thpu²⁻ and Hthpu⁻ in the compound have hydrogen bonding moieties. Hendrickson et al. have been also reported that the compound **1** possess an abundance of potential sites for intermolecular hydrogen bonding interactions.¹⁰ Therefore we focused on the compound **1** with strong intermolecular interaction for development of the photo switchable molecular solids.

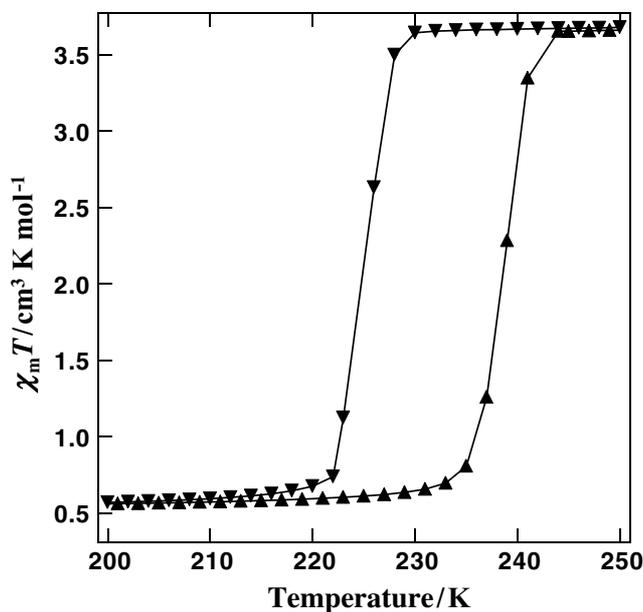


Figure 3. $\chi_m T$ versus T plots for **1**. Sample was cooled from 250 K to 200 K (\blacktriangledown) and then warmed from 200 K to 250 K (\blacktriangle) at a rate of 2 K min^{-1} .

A Hg-Xe lamp ($\lambda \approx 400\text{--}600 \text{ nm}$, 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 20 K, an increase in the dc susceptibility was observed (Figure 5). The change in the magnetization persisted for several hours at 20 K, even after the illumination was stopped. This increase suggests that a transition from the LS state to the HS state can be induced by illumination. When the temperature is raised slowly, the energy barrier between HS and LS states vanishes and light-induced metastable HS state relaxes to LS state. The relaxation temperature $T_c(\text{LIESST})$ ¹⁴ for **1** is

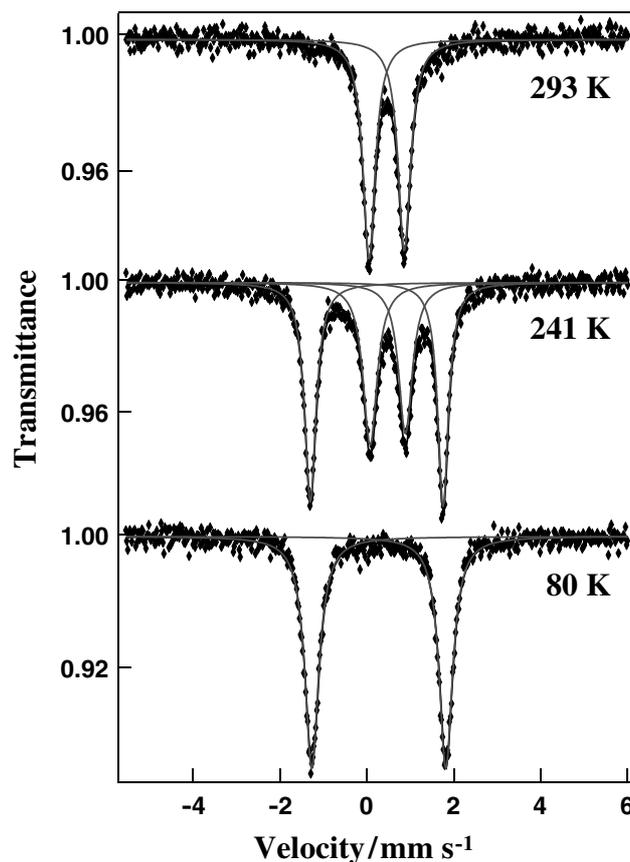


Figure 4. Mössbauer spectra for **1** at selected temperatures.

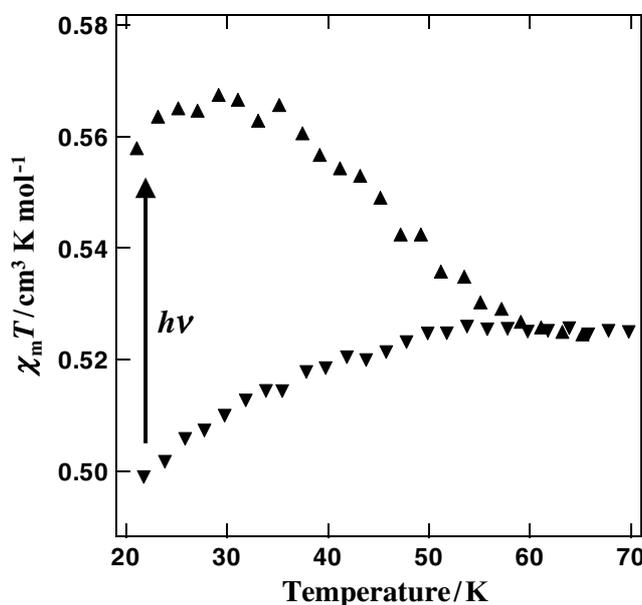


Figure 5. The $\chi_m T$ versus T plot was recorded in the warming mode (\blacktriangle) after the sample was exposed to light for 2 hour.

40 K. The achievement of an anomalous long-lived metastable state is considered to be due to the presence of the strong intermolecular interaction, and the LIESST effect for **1** with intermolecular hydrogen bonds is the second example following that for [Fe(pap)₂]ClO₄·H₂O with intermolecular π - π interaction.

In summary, we have succeeded in observing the LIESST effect for an iron(III) compound [Fe(thpu)(Hthpu)] with intermolecular hydrogen bonds. We believe that our approach, i.e., the introduction of strong intermolecular interactions to trap the metastable HS state can be applied in the design of metal complexes with LIESST effects.

Acknowledgment. This work was supported by Casio Foundation and Tokuyama Foundation.

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