First Observation of Light-Induced Excited Spin State Trapping for an Iron(III) Complex

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There has been a great interest in developing novel molecular compounds whose physical properties can be controlled by illumination.[1−11] However, until now, the number of the optically switchable molecular solids reported has been quite small. This is because the strategy to achieve photoinduced switching in a solid state system is yet to be clarified. One of the requisites of optically switchable compounds is that they have nearly degenerate electronic states. Furthermore, it is known that the structural change accompanied with the switching phenomena should not be too large, because steric effects often prevent the photochemical transformation. However, even if these requirements are satisfied, most never show photoinduced switching with long-lived metastable states. This is because, although it is possible to produce a metastable state in such compounds by illumination, the metastable state rapidly relaxes back to the stable state as a result of tunneling effects due to the small structural change. It has been reported that the photoinduced iron(III) high-spin states rapidly revert to the original low-spin states by tunneling.[12−15]

Hence, to develop a variety of optically switchable molecular solids, strategies to prevent such a rapid relaxation from a metastable state to a ground state should be developed. We propose the introduction of strong intermolecular interactions in molecular compounds. It is thought that the cooperativity resulting from the intermolecular interaction operates to increase the activation energy for the relaxation processes, enabling the observation of a long-lived metastable state after illumination.[5,6,16,17] Based on this strategy, we have succeeded in observing light-induced excited spin state trapping (LIESST) effects for an iron(III) complex for the first time.

Cooperativity can be achieved by using $\pi-\pi$ interactions as well as by using bridging ligands.[18−22] The iron(III) complex we focused on is $[Fe(pap)_2]ClO_4{\cdot}H_2O$ (hereafter designated as complex **1**), where Hpap is a tridentate Schiff-base.[23,24] The planar ligand, pap, with corresponding π electrons, has a potential ability to interact with neighboring ligands by $\pi-\pi$ interactions. In fact, the presence of a strong intermolecular interaction is suggested from the single-crystal X-ray analysis. Single crystals suitable for X-ray diffraction of **1** were isolated by slow diffusion in methanolic solutions. The complex **1** crystallizes in the triclinic P-1 space group at room temperature (Figure 1).[25] The values of the bond lengths are consistent with those typical for high-spin iron(III) compounds. Two tridentate ligands are found to be perpendicular to one another. $[Fe(pap)_2]^+$ cations form short contacts (3.50 Å) through the pyridine and phenyl rings in the ligands on an *ab* plane, providing a 2-D sheet extended by the $\pi-\pi$ interactions. 2-D sheets align along *c* axis. Water molecules and perchlorate ions exist between the 2-D sheet and are hydrogen-bonded to each other. Molecular packing of **1** is very tight. This suggests that there are strong intermolecular interactions in the molecular assembly. It should be noted that the structure of complex **1** has no remarkable features at the single molecule level compared with other typical iron(III) spin-crossover complexes.

Magnetic properties show that the value of $\chi_m T$ for **1** at room temperature is equal to 3.9 cm^3 K mol^{-1}, which corresponds to what is expected for the high-spin state in iron(III) compounds (Figure 2). On cooling, the value of $\chi_m T$ drops abruptly around $T_{1/2}{\downarrow} = 165$ K. The $\chi_m T$ value at 100 K is equal to 0.51 cm^3 K mol^{-1}, representing the low-spin state. In the warming mode, an abrupt variation of $\chi_m T$ was observed around $T_{1/2}{\uparrow} = 180$ K. Fairly abrupt transitions with a hysteresis loop (~15 K) show the presence of the strong cooperative interaction. Another important characteristic is that this complex exhibits a frozen-in effect.[8,24,26,27] This property is observed when the cooperativity is large and, hence, the relaxation rate is quite slow. These experimental results show that strong cooperative interactions operate in this compound.

A Hg−Xe lamp was used as a light source. Hauser et al. reported that the excitation of the spin-allowed ligand-to-metal charge transfer (LMCT) band results in the transient generation of high-spin iron(III) fractions.[12,13] Hence, to excite the LMCT

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(25) Crystallographic study of **1**. X-ray crystallographic data for **1** at room temperature ($C_{24}H_{20}O_7N_4Cl_1Fe_1$):_ FW = 567.74, brown platelet (0.3 × 0.3 × 0.03), triclinic, space group *P*1, $a = 11.051(5)$ Å, $b = 11.635(6)$ Å, $c = 9.878(4)$ Å, $\alpha = 105.95(1)°$, $\beta = 91.59(2)°$, $\gamma = 79.69(2)°$, $V = 1201.1(10)$ Å^3, $Z = 2$, $D_{calcd} = 1.570$ gcm^{-3}. The structure was solved by direct methods and expanded using Fourier techniques. The refinements by full matrix least-squares gave an *R* factor of 0.0725 and a weighted *R* factor (R_w) of 0.1004 from 1720 reflections with intensity $I > 3\sigma(I)$ for 335 variables; linear absorption coefficient μ(Mo K_α) = 7.9 cm^{-1}. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined.

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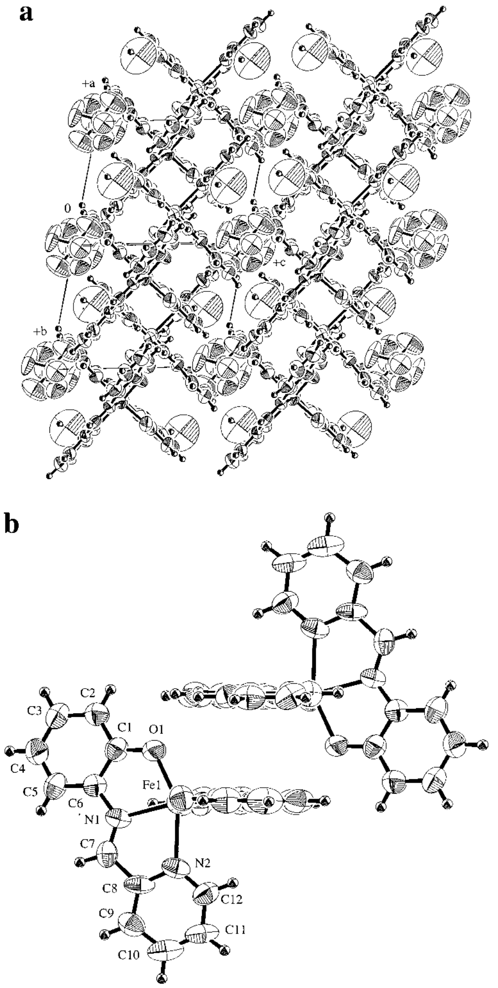

Figure 1. Molecular structures in the high-spin state (room temperature). (a) Projection of the crystal structure of **1**. (b) Structure of the $\pi-\pi$ stucking between complexes.

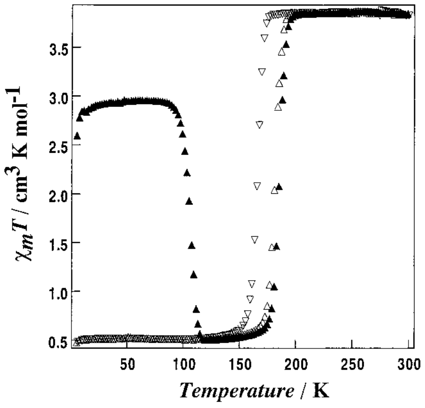

Figure 2. $\chi_m T$ versus T plots for **1**. Sample was cooled from 300 to 5 K (▽) and then warmed from 5 to 300 K (△) at a rate of 2 K min^{-1}. Sample was warmed at a rate of 2 K min^{-1} after it was quenched to 5 K (▲).

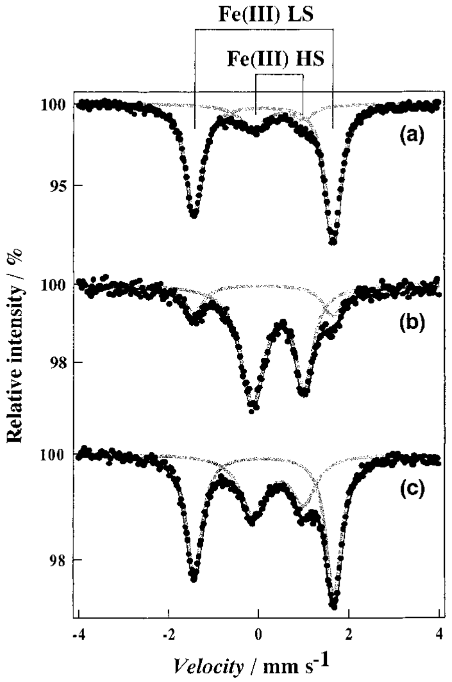

Figure 3. ^{57}Fe Mössbauer spectra for **1** at 13 K. (a) Spectrum before illumination. (b) Spectrum after illumination. (c) Spectrum after thermal treatment at 130 K.

band of complex **1**, the light (400−600 nm) passing through a combination of IR cutoff and green filters was guided via a optical fiber into the SQUID magnetometer. When the sample was illuminated at 5 K, the increase of the magnetization value was observed. This suggests that the transition from low-spin to high-spin was induced by illumination. The change in the magnetization persisted for periods of at least 10 h after the illumination was stopped. Mössbauer spectrum in Figure 3a measured before illumination at 13 K reveals a wide quadrupole-split doublet (ΔQ = 3.08 mm s^{-1}; isomer shift δ = 0.11 mm s^{-1}), representing the low-spin state. The spectrum measured after illumination for 15 min shows a narrow quadrupole-split doublet (ΔQ = 1.14 mm s^{-1}, δ = 0.44 mm s^{-1}), representing the high-spin state. Thus, it has been confirmed that the low-spin moieties changed to the high-spin state by illumination. By analogy to previous work, it is thought that the visible light illumination of complex **1** induces the LMCT, followed by relaxation to the high-spin state. When the temperature is raised to 130 K for a few minutes and is again lowered to 13 K, the metastable state is found to have relaxed back to the low-spin ground state (ΔQ = 3.08 mm s^{-1}; δ = 0.11 mm s^{-1}). The metastable state could be maintained for a long time, provided that the sample was kept below ~70 K. The achievement of an anomalous long-lived metastable state is considered to be due to the presence of the strong intermolecular interaction, because, as described above, complex **1** is a conventional compound at the single-molecule level. It is important to note that the LIESST effect has been believed to be impossible for an iron(III) complex due to the small structural change associated with the spin transition.[7]

In summary, we have succeeded in observing the LIESST effect for an iron(III) complex for the first time. We believe that our approach, that is, the introduction of intermolecular interactions to trap the metastable state, can be widely applied not only in the design of other metal complexes with LIESST effects but also in the design of a variety of optically switchable molecular compounds.

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Supporting Information Available: Tables giving crystallographic data, positional parameters, and *U* values for **1** (PDF). X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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