COMMUNICATION

ChemComm
www.rsc.org/chemcomm

An abrupt spin transition based on short S···S contacts in a novel Fe(II) complex whose ligand contains a 1,3-dithiole ring

Kazuyuki Takahashi,[a] Tomoko Kawakami,[ab] Zhong-ze Gu,[a] Yasuaki Einaga,[b] Akira Fujishima[c] and Osamu Sato*[a]

[a] *Kanagawa Academy of Science and Technology (KAST), KSP Bldg. East 412, 3-2-1 Sakado, Takatsu-ku, Kawasaki, Kanagawa 213-0012, Japan. E-mail: sato@fchem.chem.t.u-tokyo.ac.jp*

[b] *Department of Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Yokohama 223-8522, Japan*

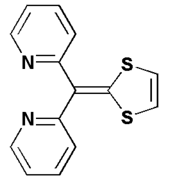
[c] *Department of Applied Chemistry, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

Received (in Cambridge, UK) 15th July 2003, Accepted 8th August 2003
First published as an Advance Article on the web 19th August 2003

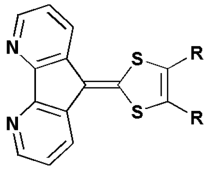
The first preparation of an Fe(II) spin-crossover complex including a 1,3-dithiole ligand is reported. Crystal analyses of both the low- and the high-temperature phases reveal that short S···S contacts play a key role in an abrupt spin transition.

Molecular switching materials have recently aroused a great deal of attention in the field of materials science. Spin-crossover (SC) complexes, which can exhibit a spin transition between the low-spin (LS) and the high-spin (HS) states due to an external perturbation such as temperature, pressure or light, belong in this class of materials.[1–4] Since the first discovery of the light-induced excited spin state trapping (LIESST) effect in an Fe(II) SC complex,[5] the photo-induced magnetization of SC complexes has been extensively studied, not only due to scientific interest, but also because of the potential for optical magnetic memory and display material applications. In order to realize such a switching phenomenon in an SC complex, a hysteresis loop and an abrupt change in the magnetization curve are considered to be the most important requirements, because these two phenomena can be assumed to be evidence that a cooperative effect works throughout the solid. In general, cooperativity in molecular solids is derived from intermolecular interactions such as π–π interactions,[6–9] hydrogen bonding,[10,11] coordination bonding,[12–14] and so on. It should be noted that the unusually long-lived light-induced HS state in the Fe(III) SC complex, $[\mathrm{Fe(III)(pap)_2}](\mathrm{ClO_4})$, was firstly observed on the basis of such strong intermolecular π–π interactions,[15] although the difficulty in achieving the LIEEST effect in Fe(III) SC complexes had been predicted theoretically.[3] In this context, we have focused our attention upon another intermolecular interaction, namely an inter-chalcogen-atom interaction, which is often seen in molecular-based conductors. This interaction is not only an attractive interaction but also has the potential to be a path for an electrical current. Thus, we would like to introduce a 1,3-dithiole (DT) ring into the ligand of the well-known $\mathrm{Fe(II)(L)_2(NCX)_2}$-type SC systems, where L is an N,N-bidentate ligand. So far, several diazafluorenylidene derivatives (DazfDTs) have been recognized as ligands that contain both a 1,3-dithiole and pyridine rings.[16,17] However, these ligands were generally insoluble in common solvents due to their rigid planar structures. Therefore, we have designed DPyDT, which stands for di(2-pyridyl)methylidene-1,3-dithiol-2-ylidene, as a more flexible ligand for the Fe(II) SC complex. We report herein on its preparation and of the abrupt SC behavior of the novel complex, $\mathrm{Fe(II)(DPyDT)_2(NCS)_2{\cdot}0.5MeOH}$. To the best of our knowledge, this is the first Fe(II) SC complex whose ligand has a 1,3-dithiole ring. Furthermore, crystal structural analyses in both the LS and the HS states clearly indicate cooperativity in solid, which can mainly be attributed to the inter-chalcogen-atom interaction in both the LS and HS states. The LIESST effect was also studied in this complex.

DOI: 10.1039/b308070f



DPyDT



DazfDTs

The ligand molecule DPyDT was synthesized by a Wittig reaction. That is, a 1,3-dithiolium salt in THF was treated by tributylphosphine for 1 h at rt to form the phosphonium salt *in situ*. The addition of di(2-pyridyl)ketone to this solution was followed by treatment with BuLi at −78 °C to afford DPyDT in 43% yield as a pale yellow solid. All the spectral data of the new ligand are in good agreement with its structure.† The Fe(II) complex, $\mathrm{Fe(DPyDT)_2(NCS)_2{\cdot}0.5MeOH}$, was obtained as an orange powder by adding a methanolic solution of KSCN to the mixture of the ligand and the iron(II) chloride in methanol under Ar atmosphere. Although we tried to measure the electrical conductivity of the present complex, it proved to be an insulator. On cooling with liquid N_2, the color of the complex changed from orange to red and on warming to rt the reverse color change was observed, suggesting that a spin transition between the HS and LS states might occur. Actually, at 300 K the absorption maxima of the present Fe(II) complex was at 450 nm in the visible region. On the other hand, at 6 K an additional peak was observed at around 570 nm. In order to confirm the spin-crossover phenomenon, the temperature dependence of $\chi_M T$ (where χ_M is the molar magnetic susceptibility and T is temperature) of a crystalline sample of this complex was measured using a Quantum Design MPMS-5S SQUID susceptometer, as shown in Fig. 1. At rt the $\chi_M T$ value is 3.1 cm^3 K mol^{-1}, indicating that the complex is almost all in the HS state. On decreasing the temperature, a very abrupt change in $\chi_M T$ was observed at around 130.5 K($T_{1/2}\downarrow$). This transition was complete within 3 K. Afterwards the spin transition, $\chi_M T$ value is almost 0, indicating it is in the LS state. On heating the sample, the reverse transition occurred at 132.5 K($T_{1/2}\uparrow$), resulting in a narrow hysteresis loop (about 2 K). However, this abrupt spin transition and narrow hysteresis loop suggest that a strong cooperative interaction between molecules exists in this complex.

Fortunately, the crystal structures of the Fe(II) complex could be determined in both the LS state at 103 K and the HS state at 160 K.‡ The space group did not change before and after the spin transition. The molecular arrangement, with numbering of the selected atoms at 160 K, is shown in Fig. 2. The coordination mode of the isothiocyanate anion is the *cis*-conformation, as is often seen in $\mathrm{Fe(L)_2(NCS)_2}$ complexes. Remarkable differences in the coordination bond lengths between iron and nitrogen atoms and the intermolecular S···S distances between both phases are observed. The average coordination bond lengths between Fe(II) and nitrogen atoms at ligands and isothiocyanate anions are 2.191(3) and 2.107(4) Å at 160 K, and 1.996(4) and 1.965(5) Å at 103 K, respectively. These values are consistent with those in the crystal structures of $Fe(phen)_2(NCS)_2$ in both spin states.[18] This clearly means that the complex is in the LS state at 103 K and is in the HS state at 160 K. There are two kinds of short S···S contacts at 160 K. The first of these is 3.542 Å between S(1) in the ligand and S(5′) in the isothiocyanate anion and the second is found between ligand molecules (S(2)···S(3), 3.689 Å), to form the one-dimensional chain-like structure. On the other hand, a third short S···S contact appears at 103 K. The first and second short contacts are in the same relative positions as observed in the high temperature phase. However, the second one is at 3.573(2) Å, which is much shorter than it is in the high temperature phase. The third short contact, S(4″)···S(6), at 3.689(3) Å was discovered between the one-dimensional chains above mentioned. This means that a two-dimensional S···S network is constructed in the low temperature phase. In addition, no other interactions ever exist in both phases. This fact suggests that these relatively strong S···S interactions play a key role in the abrupt spin transition.

The LIESST experiment was carried out on a ground sample of the complex with an adhesive transparent tape (Fig. 3). On illumination with a YAG laser (532 nm) at 5 K, the $\chi_M T$ value of the complex gradually increased, suggesting that the metastable HS state could be trapped in this complex. Finally, $\chi_M T$ reached a value of 3.0 cm^3 K mol^{-1}, indicating the almost complete conversion of the LS state into the metastable HS state. In heating mode, the value of $\chi_M T$ began to decrease at 60 K, and then completely relaxed to the ground LS state at 70 K (T(LIESST) = 66 K).

In summary, a novel Fe(II) spin-crossover complex including a 1,3-dithiole ring was prepared. The cooperative phenomenon was found to be derived mainly from short S···S contacts. In order to introduce conducting properties into a spin crossover system, further extension of the π-system on the ligand part is currently in progress.

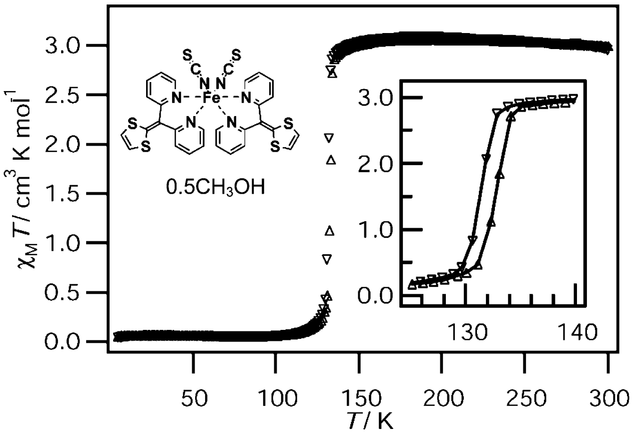


Fig. 1 $\chi_M T$ *vs.* T plot for $Fe(DPyDT)_2(NCS)_2\cdot0.5CH_3OH$ (a crystalline sample). Cooling and warming rate is 1 K min^{-1}.

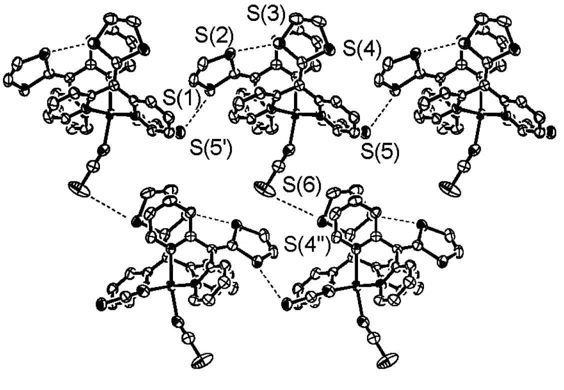


Fig. 2 Crystal structure of $Fe(DPyDT)_2(NCS)_2\cdot0.5CH_3OH$ at 160 K.

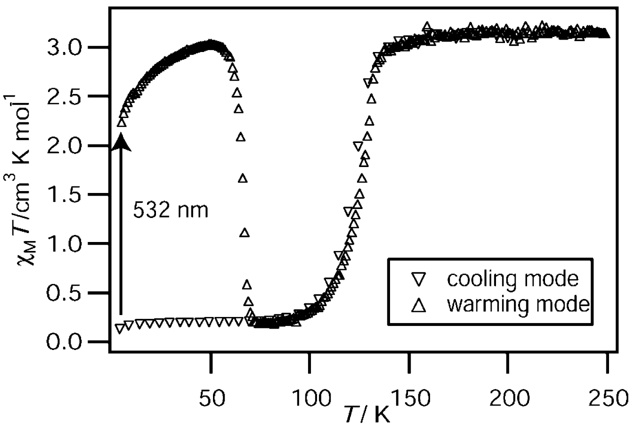


Fig. 3 $\chi_M T$ *vs.* T plot for $Fe(DPyDT)_2(NCS)_2\cdot0.5CH_3OH$ (a ground sample). Cooling and warming rate is 1 K min^{-1}.

We gratefully acknowledge financial support of this work by the Nissan Science Foundation.

Notes and references

† DPyDT: mp 113.0–114.0 °C, ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.76(d, 2H, J = 4.9 Hz), 7.65(m, 2H), 7.14(m, 2H), 7.08(d, 2H, J = 7.9 Hz), 6.51(s, 2H) ppm, UV-vis (CH_2Cl_2) λ_{max} 214, 384 nm, Mass m/z 270(M$^+$), Anal calcd for $C_{14}H_{10}N_2S_2$: C, 62.19; H, 3.73; N, 10.36: found: C, 62.44; H, 3.86; N, 10.10%.

‡ Crystal data for $Fe(DPyDT)_2(NCS)_2\cdot0.5CH_3OH$: $C_{30.5}H_{22}N_6S_6FeO_{0.5}$, M = 728.76; T = 160 K, monoclinic, space group $P2_1/c$ (no. 14), a = 10.7461(7), b = 19.931(2), c = 15.203(1) Å, β = 104.661(3) °, V = 3150.0(4) Å^3, Z = 4, D_{calc} = 1.537 g cm^{-3}, μ(Mo–Kα) = 9.11 cm^{-1}, 22794 reflections measured, 6584 unique (R_{int} = 0.066), final $R1$ = 0.062 ($I > 2.0\sigma(I)$), $wR2(F^2)$ = 0.114 (all data); T = 103 K, monoclinic, space group $P2_1/c$ (no. 14), a = 10.7363(8), b = 19.901(2), c = 14.777(1) Å, β = 103.847(3) °, V = 3065.5(4) Å^3, Z = 4, Dcalc = 1.579 g cm^{-3}, μ(Mo–Kα) = 9.36 cm^{-1}, 16504 reflections measured, 6299 unique (R_{int} = 0.070), final $R1$ = 0.073 ($I > 2.0\sigma(I)$), $wR2(F^2)$ = 0.160 (all data). CCDC 215599 and 215600. See http://www.rsc.org/suppdata/cc/b3/b308070f/ for crystallographic data in .cif or other electronic format.

1 E. König, *Coord. Chem. Rev.*, 1968, **3**, 471.
2 P. Gütlich, *Struct. Bonding (Berlin)*, 1981, **44**, 83.
3 P. Gütlich, A. Hauser and H. Spiering, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 20.
4 P. Gütlich, Y. Garcia and H. A. Goodwin, *Chem. Soc. Rev.*, 2000, **29**, 419.
5 S. Decurtins, P. Gütlich, C. P. Köhler, H. Spiering and A. Hauser, *Chem. Phys. Lett.*, 1984, **105**, 1.
6 J.-F. Létard, P. Guionneau, E. Codjovi, O. Lavastre, G. Bravic, D. Chasseau and O. Kahn, *J. Am. Chem. Soc.*, 1997, **119**, 10861.
7 J.-F. Létard, P. Guionneau, L. Rabardel, J. A. K. Howard, A. E. Goeta, D. Chasseau and O. Kahn, *Inorg. Chem.*, 1998, **37**, 4432.
8 Z. J. Zhong, J.-Q. Tao, Z. Yu, C.-Y. Dun, Y.-J. Liu and X.-Z. You, *J. Chem. Soc., Dalton Trans.*, 1998, 327.
9 S. Hayami, Z.-Z. Gu, H. Yoshiki, A. Fujishima and O. Sato, *J. Am. Chem. Soc.*, 2001, **123**, 11644.
10 M. Mikami, M. Konno and Y. Saito, *Acta Cryst.*, 1980, **B36**, 275.
11 S. Hayami, Z.-Z. Gu, Y. Einaga, Y. Kobayasi, Y. Ishikawa, Y. Yamada, A. Fujishima and O. Sato, *Inorg. Chem.*, 2001, **40**, 3240.
12 T. Kitazawa, Y. Gomi, M. Takahashi, M. Takeda, M. Enomoto, A. Miyazaki and T. Enoki, *J. Mater. Chem.*, 1996, **6**, 119.
13 V. Niel, J. M. Martinez-Agudo, M. C. Muñoz, A. B. Gaspar and J. A. Real, *Inorg. Chem.*, 2001, **40**, 3838.
14 V. Niel, M. C. Muñoz, A. B. Gaspar, A. Galet, G. Levchenko and J. A. Real, *Chem. Eur. J.*, 2002, **8**, 2446.
15 S. Hayami, Z.-Z. Gu, M. Shiro, Y. Einaga, A. Fujishima and O. Sato, *J. Am. Chem. Soc.*, 2000, **122**, 7126.
16 K. Sako, M. Kusakabe and H. Tatemitsu, *Mol. Cryst. Liq. Cryst.*, 1996, **285**, 101.
17 K. Sako, Y. Misaki, M. Fujiwara, T. Maitani, K. Tanaka and H. Tatemitsu, *Chem. Lett.*, 2002, 592.
18 B. Gallois, J.-A. Real, C. Hauw and J. Zarembowitch, *Inorg. Chem.*, 1990, **29**, 1152.