

Spin Crossover and Light-induced Excited Spin-state Trapping Observed for an Iron(II) Complex Chelated with Tripodal Tetrakis(2-pyridyl)methane

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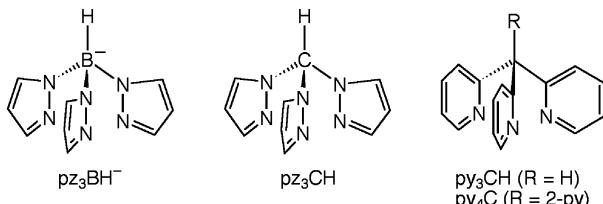
(Received March 4, 2012; CL-120187; E-mail: ishi@pc.uec.ac.jp)

A novel iron(II) complex $[\text{Fe}(\text{py}_4\text{C})_2][\text{Fe}(\text{py}_4\text{C})(\text{NCS})_3]_2$ was synthesized, where py_4C stands for tetrakis(2-pyridyl)methane. Spin crossover occurred at 161 K ($T_{1/2}$). Light-induced excited spin-state trapping was observed when irradiated with 532 nm at 10 K, and the conversion was 89%. The relaxation took place at 58 K on heating.

Spin crossover (SCO) is a reversible low-spin–high-spin transition by external stimuli such as heat and light.^{1,2} Although various bis-tripodal iron(II) SCO complexes involving hydro-tris(1-pyrazolyl)borate (pz_3BH^-) have well been studied,³ the corresponding tris(1-pyrazolyl)methane (pz_3CH) compounds are rather rare (Scheme 1).⁴ To our knowledge, there has been only one report on tris(2-pyridyl)methane (py_3CH) complex toward development of SCO compounds⁵ (the 2-pyridyl group is abbreviated as py hereafter).

Oda and co-workers have exploited a unique skeleton tetrakis(2-pyridyl)methane (py_4C),⁶ which can serve as bi- and tridentate chelating and/or bridging ligands, and actually the Ag^+ , Cu^{2+} , Co^{2+} , and Fe^{2+} complexes were synthesized.⁷ The Co^{2+} complex exhibited SCO behavior.^{7b} We have reported py_4C -bridged dinuclear Mn^{2+} and Ni^{2+} complexes⁸ from the magnetic interest owing to the spiro-junctioned D_{2d} symmetry. For the development of SCO materials, $[\text{Fe}(\text{py}_4\text{C})_n]^{2+}$ compounds will be an attractive target. We will report here distinct SCO and LIESST (light-induced excited spin-state trapping)⁹ behavior on a novel iron(II) coordination compound $[\text{Fe}(\text{py}_4\text{C})_2][\text{Fe}(\text{py}_4\text{C})(\text{NCS})_3]_2$ (**1**).

Compound **1** was synthesized by simply mixing methanol solutions (50 mL in total) containing $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (31 mg, 0.16 mmol), LiNCS (60%, 56 mg, 0.52 mmol), and py_4C (62 mg, 0.19 mmol) in the presence of L-ascorbic acid (5 mg) under nitrogen. The mixture was allowed to stand in a refrigerator for three days, giving **1** as reddish orange polycrystalline precipitates. The products were separated on a filter and dried under reduced pressure. The yield was 61%. The elemental analysis supported the formula, and the IR spectrum showed absorptions characteristic of thiocyanate and py_4C .¹⁰



Scheme 1. Structural formulas of pz_3BH^- , pz_3CH , py_3CH , and py_4C .

The X-ray crystal structure of **1** was determined at 100 K.¹¹ Figure 1 shows the molecular structures of the $[\text{Fe}(\text{py}_4\text{C})(\text{NCS})_3]^-$ and $[\text{Fe}(\text{py}_4\text{C})_2]^{2+}$ moieties in **1**. The Fe1 ion is surrounded by the six nitrogen atoms from one tridentate py_4C ligand and three NCS anions. The Fe1-N distances are 1.924(3)–1.984(3) Å, which are characteristic of a low-spin Fe^{2+}N_6 coordination structure.¹² The Fe2 ion in $[\text{Fe}(\text{py}_4\text{C})_2]^{2+}$ is located at the crystallographic inversion center and surrounded by the six nitrogen atoms from two py_4C ligands. The six py rings are approximately related with an S_6 symmetry, but the actual space group is $P\bar{1}$ owing to the peripheral py group. The Fe2-N bond lengths (1.952(3)–1.979(3) Å) fall in a typical range of a low-spin Fe^{2+}N_6 octahedron.¹² The hydrogen atoms were experimentally found, and the uncoordinated py groups were proven to show no disorder.

After being heated to 240 K, the X-ray crystallographic analysis on the same crystal was also successful, thanks to a single-crystal-to-single-crystal structural transformation. The bond lengths are somewhat elongated in the same space group;

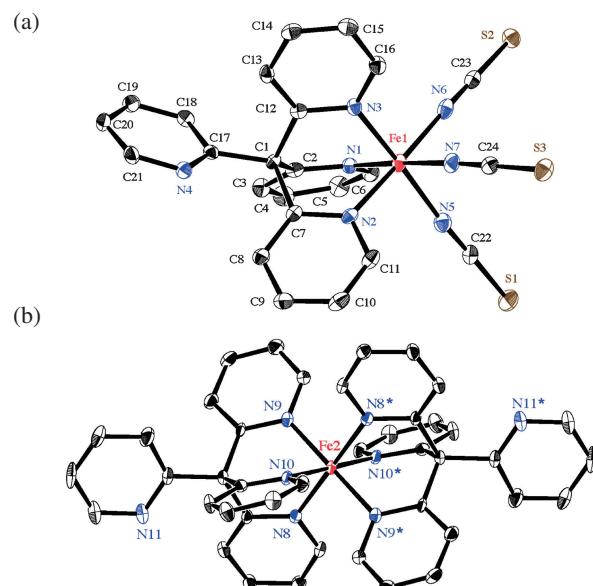


Figure 1. X-ray crystal structure of (a) $[\text{Fe}(\text{py}_4\text{C})(\text{NCS})_3]^-$ and (b) $[\text{Fe}(\text{py}_4\text{C})_2]^{2+}$ moieties in **1** measured at 100 K. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted. Selected bond distances at 100 K: Fe1-N1 , 1.957(3); Fe1-N2 , 1.984(3); Fe1-N3 , 1.924(3); Fe1-N5 , 1.960(4); Fe1-N6 , 1.973(3); Fe1-N7 , 1.963(3); Fe2-N8 , 1.979(3); Fe2-N9 , 1.964(3); Fe2-N10 , 1.952(3) Å. At 240 K: Fe1-N1 , 2.195(4); Fe1-N2 , 2.286(4); Fe1-N3 , 2.133(4); Fe1-N5 , 2.075(5); Fe1-N6 , 2.148(4); Fe1-N7 , 2.094(4); Fe2-N8 , 1.980(4); Fe2-N9 , 1.961(3); Fe2-N10 , 1.949(3) Å.

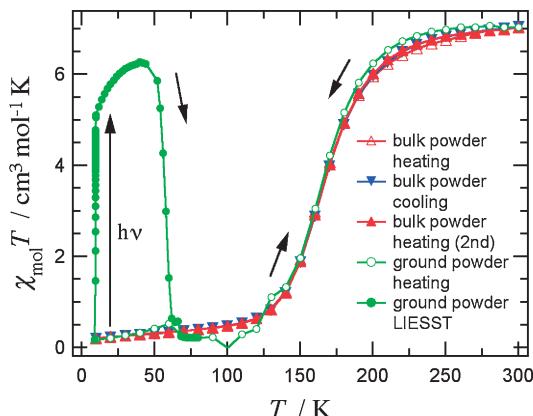


Figure 2. The $\chi_{\text{mol}}T$ vs. T plots for a polycrystalline specimen of **1** (triangles). Temperature scan sequences are denoted in a legend as heating (10 to 400 K), cooling (400 to 10 K), and heating (2nd). The region 300 to 400 K is not shown. The results of the LIESST on a finely ground specimen of **1** before and after illumination are superposed (circles).

the Fe1–N distances (2.075(5)–2.286(4) Å) are ca. 10% longer than those of the low-temperature phase and typical of a high-spin Fe^{2+}N_6 structure.¹² On the other hand, the Fe2–N distances (1.949(3)–1.980(4) Å) are practically unchanged from those of the low-temperature phase.

The magnetic susceptibility of a polycrystalline specimen of **1** was measured on a SQUID magnetometer (Figure 2). Compound **1** behaved as a paramagnetic species involving two high-spin Fe^{2+} ions, as indicated by $\chi_{\text{mol}}T = 7.04 \text{ cm}^3 \text{ K mol}^{-1}$ at 350 K. Two Fe^{2+} ions out of three have a high-spin $S = 2$ state with $g = 2.16$. On cooling, a clear SCO transition took place at 161 K ($T_{1/2}$; defined as the temperature at the equimolar fractions of high- and low-spin species), and **1** became practically diamagnetic ascribable to a low-spin state below ca. 120 K. A heating process from 10 to 400 K reversibly showed a spin-transition of $S = 0 \rightarrow S = 2$ for two Fe^{2+} ions without any hysteresis. Repeated experiments completely reproduced the same curve.

Combining the crystallographic study results, we conclude that only the Fe^{2+} ion in $[\text{Fe}(\text{py}_4\text{C})(\text{NCS})_3]^-$ underwent SCO. The Fe^{2+} ion in $[\text{Fe}(\text{py}_4\text{C})_2]^{2+}$ exhibited a low-spin state in the entire temperature range, which was supported by parallel experiments on the related compounds such as $[\text{Fe}(\text{py}_4\text{C})_2](\text{NCS})_2 \cdot 2\text{CH}_3\text{OH}$ (**2**)¹³ etc. Anderson and co-workers have reported that $[\text{Fe}(\text{py}_3\text{CH})_2](\text{NO}_3)_2$ exhibited a full low-spin at room temperature.⁵ There has been no evidence for SCO in bis(tripodal)-type $[\text{Fe}(\text{py})_6]$ compounds,^{7b} whereas the corresponding pyrazolyl analogs, $[\text{Fe}(\text{pz}_3\text{BH})_2]$ and $[\text{Fe}(\text{pz}_3\text{CH})_2]^{2+}$ derivatives, have been well known for decades to afford many SCO compounds.^{3–5,14} The tripodal ligand py₄C can be applied to SCO study with an aid of appropriate *N*-donor ligands or anions such as thiocyanates. In the present compound, the $[\text{Fe}(\text{py}_4\text{C})(\text{NCS})_3]^-$ portion has been revealed to be a SCO building block.

We also investigated photoswitching effects of the magnetic properties of **1**. The finely ground powder specimen was nominally kept at 10 K, and the magnetic susceptibility was monitored during and after laser light illumination (532 nm).¹⁵

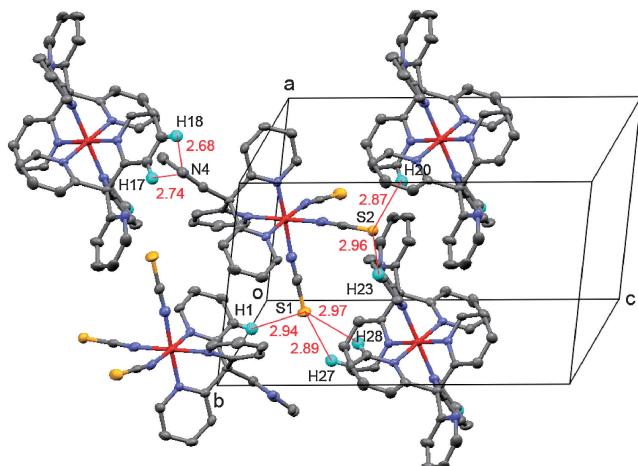


Figure 3. Molecular arrangement in the crystal of **1** measured at 100 K. Selected hydrogen atoms are drawn in light blue, and related intermolecular N···H and S···H contacts are indicated by red hairlines. The distances are shown in Å with esd's of ca. 0.02 Å.

The illumination gave rise to an increase of χ_{mol} up to 89% of the maximal value (Figure 2, filled circles). The incomplete conversion may be interpreted in terms of a photoequilibrium. The excited state was trapped in the dark below ca. 50 K. The sample chamber was then warmed, and the magnetic susceptibility was abruptly decayed at 58 K (T_{LIESST} , defined by the minimum in the $d(\chi_{\text{mol}}T)/dT$ vs. T plot¹⁶), giving the complete loss of the high-spin population. Thus, **1** was proven to be a typical LIESST compound.

Létard and co-workers reported the linear relation between $T_{1/2}$ and T_{LIESST} from the classification of the database on sixty Fe^{2+} LIESST compounds, but there have been only a few examples of *mer*-type $[\text{FeL}_2]$ compounds and no *fac*-type compound.¹⁶ The present work will provide an example for further discussion of the $T_{1/2} - T_{\text{LIESST}}$ and magneto–structure relationships.

One may wonder what role the py group free from ligation plays, since py₄C works as a tridentate ligand. The SCO features, LIESST in particular, are well-known to depend on the cooperativity; that is, on the propagation of the spin-state change from one molecule to the other throughout the material.¹ Accordingly, the peripheral substituents and counter ions are of great importance for possible intermolecular interaction,¹⁷ typically through hydrogen bonds, dipolar interaction, CH–π interaction, and π–π stacking. In the present complex, N4···H1ⁱ (2.74 Å) and N4···H18ⁱ contacts (2.68 Å; the symmetry operation code for *i* is $-x, 1 - y, 2 - z$) are notable, which are shorter than the sum of the van der Waals radii (2.75 Å)¹⁸ (Figure 3).

It has also been pointed out that the interatomic contacts around the thiocyanate sulfur atoms would be important for cooperativity.¹⁹ As Figure 3 shows, intermolecular atomic contacts (2.87–2.97 Å) were found between thiocyanate sulfur atom and py hydrogen atoms in $[\text{Fe}(\text{py}_4\text{C})_2]^{2+}$, as well as a contact at S1···H1ⁱⁱ in $[\text{Fe}(\text{py}_4\text{C})(\text{NCS})_3]^-$ (2.94 Å; the symmetry operation code for *ii* is $1 - x, -y, 2 - z$). They are slightly shorter than the sum of the van der Waals radii (3.0 Å for S···H).¹⁸ The $[\text{Fe}(\text{py}_4\text{C})_2]^{2+}$ moiety has an advantage in forming

hydrogen bonds, because the proton acidity is enhanced by the +2 charge.

In conclusion, py_4C was utilized for iron(II)-based SCO and LIESST materials. A number of LIESST compounds have been developed so far because magnetic materials presenting a stable and reversible switch are of interest for potential industrial applications. We have demonstrated that the py_4C ligand would be a promising SCO and LIESST ligand.

This work was supported by Grants-in-Aid for Scientific Research (Nos. 22350059 and 23110711) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. The authors thank Prof. Osamu Sato (Kyushu University, Japan) and Prof. Masayuki Katsuragawa (The University of Electro-Communications) for a light-guided SQUID instrumentation system.

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- 11 Selected crystallographic data of **1**. At 100 K: $\text{C}_{90}\text{H}_{64}\text{Fe}_3\text{N}_{22}\text{S}_6$, $M_r = 1813.54$, triclinic, $P\bar{1}$, $a = 11.0176(19)$, $b = 11.1980(19)$, $c = 18.000(3)$ \AA , $\alpha = 80.888(7)$, $\beta = 73.600(7)$, $\gamma = 82.900(8)$ °, $V = 2096.2(6)$ \AA^3 , $Z = 1$, $d_{\text{calcd}} = 1.437$ g cm^{-3} , $\mu(\text{Mo K}\alpha) = 0.723$ mm $^{-1}$, $R_{\text{int}} = 0.0936$, $R(F)$ ($I > 2\sigma(I)$) = 0.0510, $R_w(F^2)$ (all data) = 0.0651 for 9504 unique reflections. At 240 K: triclinic, $P\bar{1}$, $a = 11.1308(15)$, $b = 11.1654(16)$, $c = 18.2656(19)$ \AA , $\alpha = 81.503(6)$, $\beta = 74.438(6)$, $\gamma = 83.743(7)$ °, $V = 2157.1(5)$ \AA^3 , $Z = 1$, $d_{\text{calcd}} = 1.396$ g cm^{-3} , $\mu(\text{Mo K}\alpha) = 0.703$ mm $^{-1}$, $R_{\text{int}} = 0.1094$, $R(F)$ ($I > 2\sigma(I)$) = 0.0635, $R_w(F^2)$ (all data) = 0.0786, for 9756 unique reflections. CCDC 869850 and 869851.
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- 13 Compound **2** was prepared by mixing $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, LiNCS, and py_4C in a molar ratio of 1/3/2.5 in methanol under nitrogen atmosphere. Compound **2** was preferentially prepared by being kept at room temperature after concentration. IR (neat, ATR): 3400, 2050, 1585, 1462, 1431, 752 cm^{-1} . Selected crystallographic data of **2**: $\text{C}_{46}\text{H}_{40}\text{FeN}_{10}\text{O}_2\text{S}_2$, $M_r = 884.85$, triclinic, $P\bar{1}$, $a = 9.221(7)$, $b = 9.613(10)$, $c = 12.857(2)$ \AA , $\alpha = 69.46(9)$, $\beta = 73.97(10)$, $\gamma = 83.40(11)$ °, $V = 1025.5(15)$ \AA^3 , $Z = 1$, $d_{\text{calcd}} = 1.433$ g cm^{-3} , $\mu(\text{Mo K}\alpha) = 0.523$ mm $^{-1}$, $R_{\text{int}} = 0.044$, $R(F)$ ($I > 2\sigma(I)$) = 0.0446, $R_w(F^2)$ (all data) = 0.0684, and $T = 250$ K for 4554 unique reflections. The Fe–N distances (1.9535(19)–1.9847(19) \AA) are compatible with the low-spin state determined by means of magnetic study. CCDC 869852.
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