

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

Naoki Hirose, Yuya Oso, and Takayuki Ishida*

Department of Engineering Science, The University of Electro-Communications, Chofu, Tokyo 182-8585

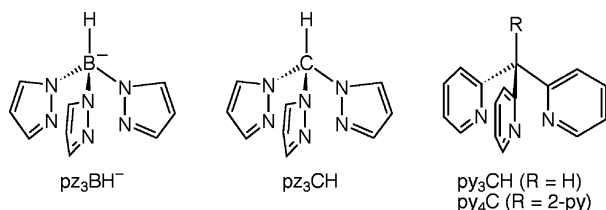
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A novel iron(II) complex $[\text{Fe}(\text{py}_4\text{C})_2][\text{Fe}(\text{py}_4\text{C})(\text{NCS})_3]_2$ was synthesized, where py_4C stands for tetrakis(2-pyridyl)methane. Spin crossover occurred at 161 K ($T_{1/2}$). Light-induced excited spin-state 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 hydrotris(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 $P1$ owing to the peripheral py group. The Fe2–N bond lengths (1.952(3)–1.979(3) Å) fell 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;

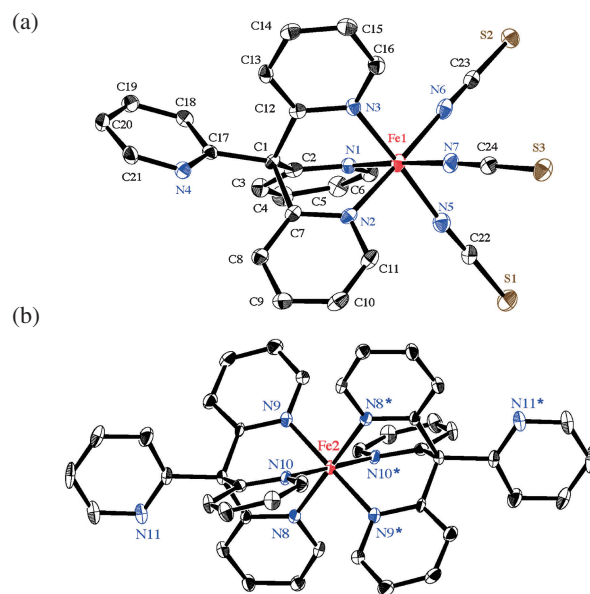


Figure 1. X-ray crystal structure of (a) $[\text{Fe}(\text{py}_4\text{C})(\text{NCS})_3]^-$ and (b) $[\text{Fe}(\text{py}_4\text{C})_2]^{2+}$ moieties in **1** measured at 100 K. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted. Selected bond distances at 100 K: Fe1–N1, 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.

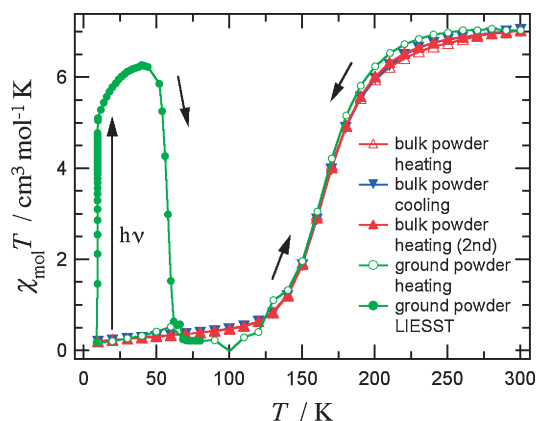


Figure 2. The $\chi_{\text{mol}}T$ vs. T plots for a polycrystalline specimen of **1** (triangles). Temperature scan sequences are denoted in a legend as heating (10 to 400 K), cooling (400 to 10 K), and heating (2nd). The region 300 to 400 K is not shown. The results of the LIESST on a finely ground 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 $[\text{Fe}(\text{pz}_3\text{CH}_2)_2]^{2+}$ derivatives, have been well known for decades to afford many SCO compounds.^{3–5,14} The tripodal ligand py_4C 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

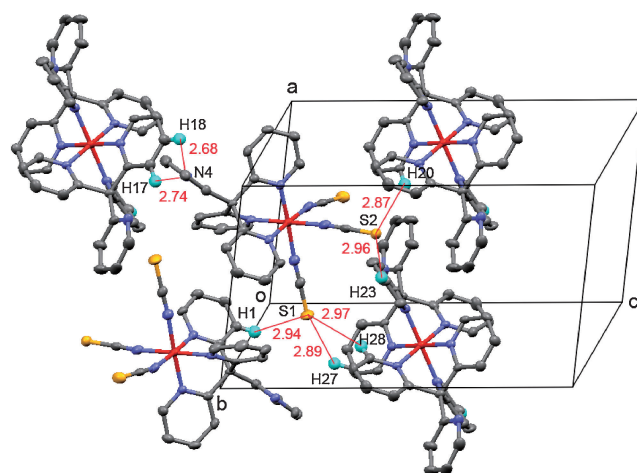


Figure 3. Molecular arrangement in the crystal of **1** measured at 100 K. Selected hydrogen atoms are drawn in light blue, and related intermolecular N...H and S...H contacts are indicated by red hairlines. The distances are shown in Å with esd's of ca. 0.02 Å.

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 py_4C 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, $\text{CH}-\pi$ interaction, and $\pi-\pi$ stacking. In the present complex, $\text{N4}\cdots\text{H17}^i$ (2.74 Å) and $\text{N4}\cdots\text{H18}^i$ 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 $\text{S1}\cdots\text{H1}^{ii}$ 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, py₄C 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 py₄C ligand would be a promising SCO and LIESST ligand.

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- 11 Selected crystallographic data of **1**. At 100 K: C₉₀H₆₄Fe₃N₂₂S₆, *M_r* = 1813.54, triclinic, *P* $\bar{1}$, *a* = 11.0176(19), *b* = 11.1980(19), *c* = 18.000(3) Å, α = 80.888(7), β = 73.600(7), γ = 82.900(8)°, *V* = 2096.2(6) Å³, *Z* = 1, *d*_{calcd} = 1.437 g cm⁻³, μ (Mo K α) = 0.723 mm⁻¹, *R*_{int} = 0.0936, *R*(*F*) (*I* > 2 σ (*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) Å, α = 81.503(6), β = 74.438(6), γ = 83.743(7)°, *V* = 2157.1(5) Å³, *Z* = 1, *d*_{calcd} = 1.396 g cm⁻³, μ (Mo K α) = 0.703 mm⁻¹, *R*_{int} = 0.1094, *R*(*F*) (*I* > 2 σ (*I*)) = 0.0635, *R*_w(*F*²) (all data) = 0.0786, for 9756 unique reflections. CCDC 869850 and 869851.
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