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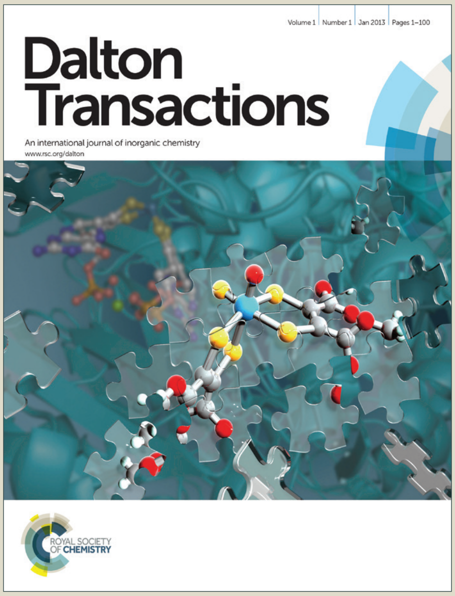

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ARTICLE

# Two-Step Magnetic Switching in a Mononuclear Iron(II) Complex around Room Temperature

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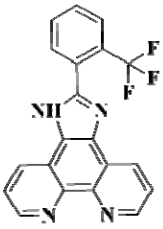
A neutral mononuclear Fe(II) complex with spin crossover (SCO) property, Fe**L**$_2$(SCN)$_2$ (1) (**L** = 2-(2-(trifluoromethyl)phenyl)-1H-imidazo[4,5-f][1,10]phenanthro-line), was solvothermally synthesized. It displays a new example of two-step SCO with $T_{c1}\downarrow$ = 250 K, $T_{c1}\uparrow$ = 260 K and $T_{c2}$ = 295 K.

## Introduction

As a consequence of the splitting of d orbitals into $t_{2g}$ and $e_g$ sets in an octahedral ligand field, transition metal ions with configurations $d^4$ to $d^7$, particularly the Fe(II) ion, can undergo spin-crossover (SCO) with appropriate ligand filed distribution and strength. The transition from diamagnetic low spin (LS) state to paramagnetic high spin (HS) state can be induced by the change of temperature or pressure, or the implementation of light or magnetic field.[1,2] However, in order to process the SCO complexes into functional devices it is expected that the material shows an abrupt and complete spin transition together with a wide thermal hysteresis around room temperature.[3] Furthermore, developing SCO materials exhibiting multi-step spin transition around room temperature, enabling a large information storage capacity, would be of great interest towards application.[4]

There are two strategies for preparing SCO complexes with thermal hysteresis.[5] The first one is based on the synthesis of 1D, 2D and 3D polymeric complexes,[6] in which Fe(II) ions are linked by rigid ligands often display abrupt SCO with hysteresis.[7] The second strategy is based on the synthesis of mononuclear complexes where Fe(II) ions are connected with each other via supramolecular interactions.[1c,8] In most cases, it is the latter class that exhibits wider hysteresis loops. Among the Fe(II) systems, the family of SCO complex [Fe(phen)$_2$(SCN)$_2$] (phen = 1,10-phenanthroline) is one of the most thoroughly studied systems.[9,10] In 1999, a new kind of Fe(II) SCO complex with 5,6-substituted 1,10-phen derivatives [Fe(dpp)$_2$(SCN)$_2$]·py (dpp = dipyrido[3,2-a:2'3'-c]phenazine, py = pyridine) was fabricated where the extended aromatic ring was expected to show strong intermolecular π-π interactions to enhance the cooperativity, which resulted in the large hysteresis (40 K) of the SCO behavior.[10]

With the aim to explore mononuclear Fe(II) system with hysteresis loop and high critical temperature, we elaborately chose 2-(2-(trifluoromethyl)phenyl)-1H-imidazo[4,5-f][1,10]-phenanthroline (**L**) (Scheme 1), which can be obtained by a one-step synthesis from 1,10-phenanthroline-5,6-dione and 2-(trifluoromethyl)benzaldehyde according to the reference reported[11]. In this communication, we report the synthesis, structures, and magnetic properties of a mononuclear Fe(II) complex Fe**L**$_2$(SCN)$_2$ (**1**). Complex **1** exhibits a new example of two-step SCO which is a combination of the gradual type and hysteresis type containing only one kind of independent Fe(II) centre with $T_{c1}\downarrow$ = 250 K, $T_{c1}\uparrow$ = 260 K and $T_{c2}$ = 295 K.[4e] Structural analysis shows that there exist three types of intermolecular interactions in complex **1**, including H-bonds, lone pair-π and π-π interaction, which suggests that cooperativity might come from the supramolecular interactions.

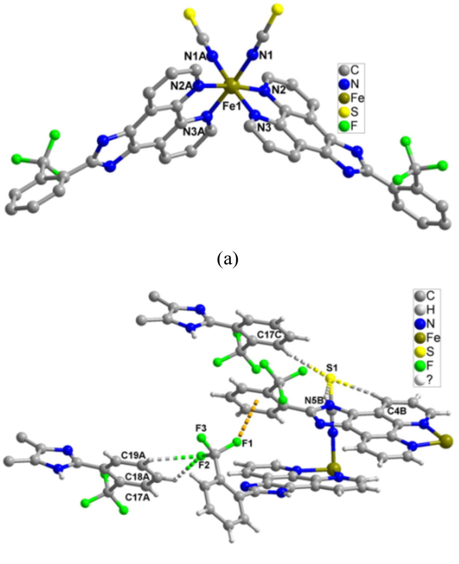


Scheme 1. Schematic representation of the ligand **L**.

## Results and discussion

Complex **1** crystallizes in the orthorhombic space group *Pbcn* at 100 K (LS state) and 420 K (HS state) (Table S1). A representation of the molecular structure of **1** at 100 K is shown in Figure 1a. Selected bond distances and angles for LS and HS of **1** are listed in Table S3. The octahedral coordination environment of the Fe(II) ion in **1** is typical for this type of

SCO complexes with six N atoms from two **L** ligands and two SCN anions. For **1** at 100 K, the Fe–N$_L$ distances in the range 1.971(3)-1.972(3) Å and Fe–N$_{SCN}$ bond lengths of 1.931(3) Å are typical of a LS Fe(II) ion (Table S3). At 420 K these coordination bond lengths increase by ca. 0.20 Å for Fe–N$_L$ and ca. 0.16 Å for Fe–N$_{SCN}$ (Table S3), demonstrating a complete SCO occurred. Between the nearest [Fe**L**$_2$(SCN)$_2$] molecules, there is a π-π stacking interaction (Fig. S2a), two kind of H-bonds (C-H…F and C-H…S) and one lone pair-π interaction (C-F…π) (Figure 1b), thus forming the 3D structure (Fig. S2b, S2c). The nearest Fe…Fe distance is 8.096 Å. According to the crystallographic data of **1** at 100 K, 230 K, 250 K, 270 K, 298 K and 420 K (discussed below), during the whole SCO process there is only one kind of independent Fe(II) centre existing in the complex.



(a)

(b)

Figure 1. (a) Molecular structure of LS **1**. (b) H-bond in LS **1**.

The temperature dependence of the magnetic susceptibility of complex **1** was examined in the range 10 to 400 K (Figure 2). At 400 K, the $\chi_m T$ value of **1** is 3.14 cm$^3$ K mol$^{-1}$, suggesting almost all of the Fe(II) centres are in the HS state. As the temperature is lowered, the $\chi_m T$ value first decreases gradually to 1.02 cm$^3$ K mol$^{-1}$ at 270 K and then descends more slowly to 0.13 cm$^3$ K mol$^{-1}$ at 220 K. Below 220 K, the $\chi_m T$ value continuously decreases to 0.07 cm$^3$ K mol$^{-1}$ at 10 K, indicating all Fe(II) centres close to the LS state. A close examination of the temperature dependence of d$\chi_m T$ /d$T$ curve revealed that the magnetic curve changes its slope with two maxima at 250 K and 295 K, respectively, which means the transition temperatures ($T_c$) $T_{c1}\downarrow$ = 250 K, $T_{c1}\uparrow$ = 260 K(Fig. S3). Upon heating, the transition temperatures are found to be $T_{c1}\uparrow$ = 260 K and $T_{c2}$ = 295 K defining a two-step SCO. The hysteresis loop of the first step is 10 K (Figure 2 inset). To the best of our knowledge, this is a new example of two-step SCO phenomenon in the mononuclear Fe(II) complex, which is a combination of the gradual type and hysteresis type and contain only one kind of independent Fe(II) centre.

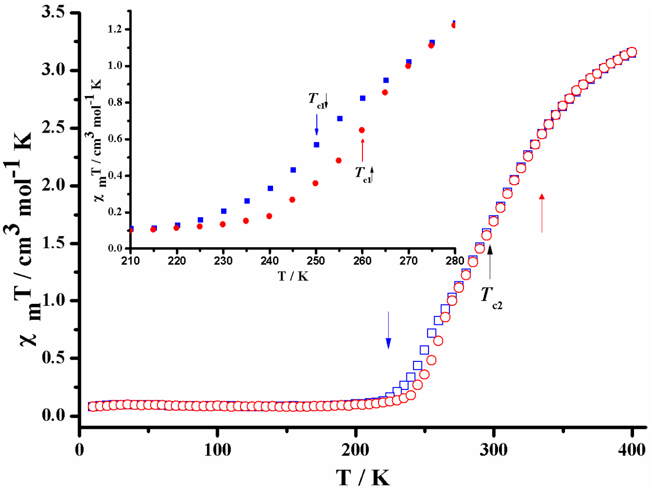


Figure 2. $\chi_m T$ vs. $T$ plots for complex **1** ($T_{c1}\downarrow$ = 250 K, $T_{c1}\uparrow$ = 260 K and $T_{c2}$ = 295 K). Inset: a zoom of hysteresis loop from 220 K to 270 K.

In order to inspect the origin of the cooperativity of complex **1**, the crystal structures at 100 K, 230 K, 250 K, 270 K, 298 K and 420 K were examined (the crystallographic data see in Table S1 and S2). As shown in Fig. S1, at 100 K, there exist lone pair-π interaction (F1…π) and the intermolecular H-bonds (C19A-H…F2, C18A-H…F2, C4B-H…S1, N5B-H…S1 and C17C-H…S1). At 230 K and 250 K, the distances of intermolecular interaction become a little longer than that at 100 K (Table 1). However, as shown in Fig. S1 and Table 1, at 270 K and 298 K, due to the different orientation of 2-(trifluoromethyl)phenyl ring, lone pair-π interaction F1…π and H-bonds C19A-H…F2 and C17C-H…S1 are disappeared, and only H-bonds C18A-H…F2, C4B-H…S1 and N5B-H…S1 are left. At 420 K, the intermolecular interactions are similar with those at 270 K and 298 K.

**Table 1.** The intermolecular interactions at 100 K, 230 K, 250 K, 270 K, 298 K and 420 K.

| Intermolecular Interactions | 100 K | 230 K | 250 K | 270 K | 298 K | 420 K |
|---|---|---|---|---|---|---|
| F1…π (F…Cg / Å) | 3.321 | 3.331 | 3.334 | -- | -- | -- |
| C17C-H…S1 (H…S / Å) | 2.858 | 2.892 | 2.893 | -- | -- | -- |
| C19A-H…F2 (H…F / Å) | 2.653 | 2.700 | 2.713 | -- | -- | -- |
| C18A-H…F2 (H…F / Å) | 2.594 | 2.642 | 2.642 | 2.404 | 2.419 | 2.431 |
| C4B-H…S1 (H…S / Å) | 2.807 | 2.816 | 2.814 | 2.877 | 2.889 | 2.938 |
| N5B-H…S1 (H…S / Å) | 2.744 | 2.765 | 2.782 | 2.721 | 2.753 | 2.915 |

As described above, it is clear that the intermolecular interactions remain identical from 100 K to 250 K and from 270 K to 420 K. Only from 250 K to 270 K, there is the obvious change of the intermolecular interactions due to the rotation of 2-(trifluoromethyl)phenyl ring. Thus, according to the variable-temperature magnetic measurement, the presence of the narrow thermal hysteresis from 220 K to 270 K could be explained by the change of the intermolecular interactions (H-bonds and lone pair-π interaction).

The differential scanning calorimetry (DSC) measurement also confirmed the two-step SCO of complex **1**. The DSC data show two peaks centred at around 267 K and 310 K in the heating mode and 257 K and 308 K in the cooling mode, respectively, corresponding to the two-step SCO (Fig. S4). The thermogravimetric analysis (TGA) data indicate that complex **1** was thermally stable up to about 320 °C (Fig. S5).

## Conclusions

We have obtained a new example of two-step SCO in the mononuclear Fe(II) system which is a combination of the gradual type and hysteresis type. Magnetic study shows that it undergoes a two-step SCO with $T_{c1}\downarrow = 250$ K, $T_{c1}\uparrow = 260$ K and $T_{c2} = 295$ K. The structure analysis of **1** at 100 K, 230 K, 250 K, 270 K, 298 K and 420 K indicates that the 10 K thermal hysteresis from 220 K to 270 K is a result of the change of the intermolecular interactions (H-bonds and lone pair-π interaction) and there is only one kind of independent Fe(II) centre during the process of SCO.

## Experimental

### Materials and synthesis

All solvents and reagents for synthesis were of analytical grade and used as received from commercial sources.

### Physical measurements

The C, H, N elemental analysis was performed on an Elementar Vario MICRO CUBE analyzer. IR spectra were measured on a NICOLET iN10 MX spectrometer with KBr pellets. Thermal analyses above room temperature were performed on a TA SDT Q600 TGA/DSC instrument at a rate of 5 °C min$^{-1}$ in air, and more accurate DSC measurements were performed on a TA Q100 DSC analyzer at 5 °C min$^{-1}$ under a nitrogen atmosphere. The X-ray powder diffraction (XRPD) spectra were recorded on a Rigaku D/Max-2400 diffractometer with the graphite monochromatized Cu Kα radiation flux at a scanning rate of 4°s$^{-1}$. Simulation of the XRPD spectra were carried out by the single-crystal data and diffraction-crystal module of the Mercury program available free of charge via the Internet at http://www.iucr.org.

The magnetic measurements were carried out on a Quantum Design PPMS-9 VSM. Susceptibility measurements were carried out in a field of 5000 Oe. All data were corrected for diamagnetism estimated from Pascal's constants and an experimental correction for the sample holder was applied.

### X-ray Data Collection and Structure Determinations

X-ray single-crystal diffraction data for complex **1** were collected on a Agilent SuperNova Dual Atlas CCD diffractometer at 100 K, 230 K, 250 K, 270 K, 298 K and 420 K with Mo Kα radiation (λ = 0.71073 Å). SAINT[12] was used for integration of the diffraction profiles. All the structures were determined by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL (semiempirical absorption corrections were applied using SADABS).[13] The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on $F^2$. The hydrogen atoms of the ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors.

### Synthetic procedures

Fe(**L**)$_2$(SCN)$_2$ (CCDC 994878 and 1054035-1054039 for 100 K, 230 K, 250 K, 270 K, 298 K and 420 K): A mixture of $FeCl_3 \cdot 6H_2O$ (0.5 mmol), **L** (0.25 mmol), KSCN (1 mmol) and $CH_3CN$ (10 mL) was sealed in a Teflon-lined stainless autoclave and heated to 160 °C for 24 hours and then cooled to room temperature over 6 hours. Black crystals were collected with 46% yield based on **L**. (Comment: the Fe$^{II}$ could result from the reduction of Fe$^{III}$ by KSCN.) Anal. Calcd (Found) for $C_{42}H_{22}F_6FeN_{10}S_2$ (%): C, 56.00 (55.84); H, 2.46 (2.49); N, 15.55 (15.32). IR bands at room temperature (w: weak, m: middle, s: strong, sh: shoulder): 3217(m), 3049(m), 2121(s), 2082(s), 1604(m), 1578(w), 1548(m), 1517(w), 1485(m), 1445(s), 1404(m), 1365(m), 1312(s), 1273(m), 1164(s), 1146(s), 1118(s), 1093(m), 1078(m), 1036(m), 955(w), 807(m), 776(m), 736(m), 727(m), 688(w), 640(w).

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## Notes and references

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† Electronic Supplementary Information (ESI) available: [crystallographic data, selected bond lengths and angles, H-bonds and lone pair-π interactions, $d\chi_mT/dT$ curve, DSC and TGA curve, XRPD]. See DOI: 10.1039/b000000x/

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