

## Research paper

## Ligand field tuned spin crossover for an iron(II)-di(diamine) system



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## ABSTRACT

Investigation of spin-crossover in iron(II)-di(diamine) system, based on ligands  $L_1$ , 4,5-dimethyl-2-(pyridine-2-yl)imidazole, has been presented in this paper. The methyl group at the adjacent sites of the donor atoms in ligand  $L_1$  can generate the crossover situation for the iron(II) tris(diimine) system. While for the iron(II)-di(diamine) system with  $L_1$ , the results are complicated: complex **1**  $\{Fe(L_1)_2(SCN)_2\}$  displays paramagnetic behavior while **2**  $\{Fe(L_1)_2(SeCN)_2\}$  is in crossover situation. The difference was attributed to the various ligand field strength of  $SCN^-$  and  $SeCN^-$ , which also resulted to the blue-shift of IR and Raman spectra, as well as red-shift and decrease in molar absorptivity of UV-Vis absorption spectrum.

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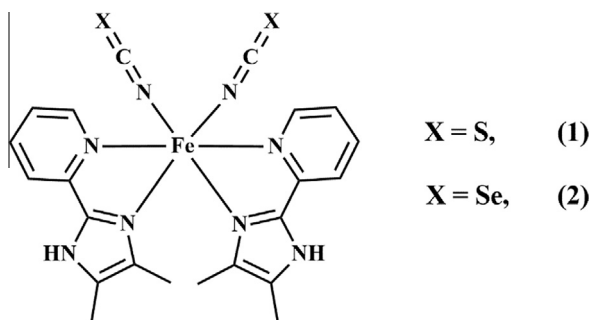
## 1. Introduction

As is one of the most impressive examples of molecular bi-stability and potential application in memory, molecular switch, sensor devices and intelligent contrast agents, the design and synthesis of molecular architectures displaying spin crossover (SCO) properties has attracted great attention over the past decade [1]. The spin transition of a SCO system between high-spin ( $HS$ ,  $^5T_2$ ) and low-spin ( $LS$ ,  $^1A_1$ ) electronic states of an octahedral  $3d^4$ – $3d^7$  transition metal complexes can be induced under such external perturbations as light irradiation, variation in temperature/pressure, or magnetic/electric fields [2], and the resulted SCO behaviors are varied as complete, incomplete, abrupt, gradual, one-step, multi-step transitions, or hysteretic [3]. To date over 200 SCO systems, many of them are interesting mononuclear  $Fe^{II}$  complexes with N-heterocyclic ligands [4] or polymeric  $Fe^{II}$  complexes with triazole or pyrazine ligands [5], as well as some  $Fe^{III}$  [6],  $Co^{II}$  [7],  $Mn^{III}$  [2b] and  $Cr^{II}$  [8] complexes, have been reported. Most of these reported SCO studies were centered on detailed structural analysis along with magnetic studies due to the key relationship between solid state structural features (intra- and intermolecular interactions) and lattice cooperativity (the extent to which spin-state changes are propagated in the solid-state). For instance, the intermolecular interactions promoting effective cooperativity [9a], the existence or absence of solvent molecules turning the spin transition behavior of the metal center [9b], and the counter anions triggering SCO transition through supramolecular host-guest binding [9c].

The iron(II) tri(diimine) system, which act as one of the most common models for spin crossover behavior due to their important feature that they can be modified readily to tune the ligand-field strength, have attracted much attention in the past years [10]. While among the diimine system, 2-(pyridin-2-yl)imidazole-related ligands has occupied a special position as ideal candidate for probing and understanding the fundamental science of spin crossover [11]. The  $[FeN_6]^{2+}$  derivative of 2-(pyridin-2-yl)imidazole was shown continuous above room temperature spin transition both in solid state and in solution [12], which was relatively early on to be a crossover system [13], thus, an appropriate variation in either their  $\sigma$ -donor and/or  $\pi$ -acceptor character of this ligand may result in crossover situation in this  $[FeN_6]^{2+}$  systems. In our other work [14], we introduced methyl group at the adjacent sites of the donor atoms ligand 2-(pyridin-2-yl)imidazole, which generated ligand  $L_1$  (4,5-dimethyl-2-(pyridine-2-yl)imidazole) and we have made a complete complexes formation of ligand  $L_1$  with different Fe (II) salts ( $Fe(ClO_4)_2$ ,  $Fe(BF_4)_2$ ,  $Fe(PF_4)_2$  and  $Fe(SbF_4)_2$ ). PPMS results revealed that these  $[FeN_6]^{2+}$  systems with  $L_1$  were all shown crossover situation, which display counter-anions-dependent transition temperatures due to interactions between counter-anions and  $L_1$ . Hence in this work, we investigated the iron(II) di(diimine) system with  $L_1$  by introduce of ligands field of  $SCN^-$  and  $SeCN^-$ , and we have obtained two new complexes  $\{Fe(L_1)_2(SCN)_2\}$  (**1**) and  $\{Fe(L_1)_2(SeCN)_2\}$  (**2**) (Scheme 1). PPMS results revealed that the **1** displays paramagnetic behavior while **2** is in complete crossover situation. Single-crystal X-ray diffraction, PXRD, TGA, Raman and IR spectra as well as UV-Vis absorption measurements (Supporting Information) were performed.

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**Scheme 1.** Molecular structures of complexes **1** and **2**.

## 2. Results and discussion

### 2.1. Crystal structure of **1** and **2**

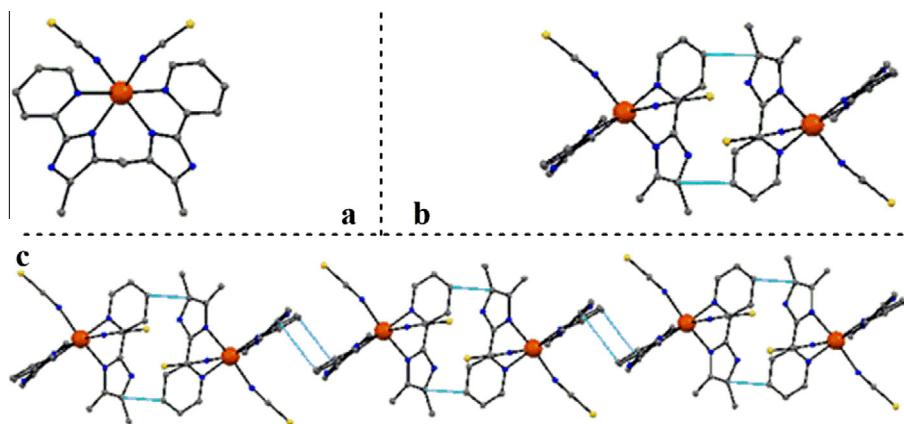
Complex **1** was crystallized from methanol solution as yellow block crystals, complex **2** was crystallized as yellowish-brown micro-crystals. The crystal structures of complexes **1** was characterized by single-crystal X-ray diffraction, and the phase purity of complex **2** was confirmed by powder X-ray diffraction. The crystal data and structure refinement for complex **1** was listed in Table S1. Complex **1** crystallizes in triclinic *P*-1 space group, the Fe<sup>II</sup> ion adopts a distorted octahedral geometry formed by four N atoms of the ligands *L*<sub>1</sub> and two N atoms of SCN<sup>-</sup>, and it displays a “butterfly-like” motif (Fig. 1a). Every two “butterfly” motif form

“di-Fe<sup>II</sup>” sites through C–H... $\pi$  (C...C distance 3.312 Å) and  $\pi$ ... $\pi$  (center...center distance 3.854 Å) contacts between adjacent *L*<sub>1</sub> ligands (Fig. 1b). The “di-Fe<sup>II</sup>” sites further packed into 1D chains through C–H... $\pi$  and  $\pi$ ... $\pi$  contacts (Fig. 1c), and the 1D chains then stacked into 3D motif (Fig. S1). For the “butterfly-like” unit, the average Fe–N distance is 2.18 Å (Table 1), and the distortion parameters  $\Sigma$  [15] is 88.05° (Table 2), typical values for a HS Fe<sup>II</sup> atom.

Shown in Fig. 2 were the PXRD profiles of complex **1** and **2** in 5–40° range, which revealed that these two complexes shown almost identical crystal lattice, demonstrating that the different magnetic properties between **1** and **2** may attribute to various ligand field of SCN<sup>-</sup> and SeCN<sup>-</sup> rather than the crystal lattice or intermolecular interactions.

### 2.2. Magnetic properties

The variable-temperature direct-current (dc) magnetic-susceptibility measurements for crystalline samples of complexes **1** and **2** were performed on a PPMS under 20000e in temperature range 400–5 K. Shown in Fig. 3 were the  $\chi_m T$  versus *T* plots of them. Complex **1** shows  $\chi_m T = 3.11 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at the room temperature, typical value for a HS Fe<sup>II</sup> atom. Upon cooling, this value kept constant until 50 K, then it undergo a gradual decrease to  $\chi_m T = 2.92 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 25 K, followed by a drop to  $1.82 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 3 K owing to the combined effect of spin-orbit coupling and zero-field splitting of the HS Fe<sup>II</sup> ion. The  $\chi_m T$  versus *T* plots of complex **2** shows a significant different behavior with **1** when the



**Fig. 1.** Crystal structures and connecting motif of complex **1**, hydrogen atoms are omitted for clarity: (a) The ASU of complex **1**; (b) The “di-Fe<sup>II</sup>” sites packed by C–H... $\pi$  and  $\pi$ ... $\pi$  contacts; (c) The 1D connecting motif of complex **1**.

**Table 1**

The bond length (Å) of the distorted octahedral geometry for **1**.

Fe–N1	Fe1–N2	Fe1–N3	Fe1–N4	Fe1–N5	Fe1–N6	Mean
2.197	2.229	2.129	2.202	2.113	2.212	2.18033333

**Table 2**

The bond angles (°) and distortion parameter ( $\Sigma$ /°) of the distorted octahedral geometry for **1**.

N1–Fe1–N2	N1–Fe1–N3	N1–Fe1–N4	N1–Fe1–N5	N2–Fe1–N3	N2–Fe1–N4	N2–Fe1–N6
106.52	90.25	75.8	87.3	93.13	82.11	75.29
N3–Fe1–N5	N3–Fe1–N6	N4–Fe1–N5	N4–Fe1–N6	N5–Fe1–N6	$\Sigma$	
98.42	87.84	90.41	106.36	91.3	88.05	

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