

# Structural Distortion Controlled Spin-Crossover Behavior

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# **Supporting Information**

**ABSTRACT:** Two mononuclear isomorphous complexes  $Fe(L1)_2(SCN)_2$  (1) and  $Fe(L2)_2(SCN)_2$  (2)  $[L1 = 2 - (pyridin-3-yl)-1H-imidazo[4,5-f]1,10-phenanthroline; L2 = 2 - (pyridin-4-yl)-1H-imidazo[4,5-f]1,10-phenanthroline] were obtained based on 1,10-phenanthroline derivatives. Due to the different structural distortion in the coordination geometries, 1 exhibits gradual spin transition around room temperature (<math>T_{1/2} = 315$  K), while 2 displays a stable high-spin state.

T he spin crossover (SCO) material has attracted considerable attention due to its fundamental importance and prospective application.<sup>1-6</sup> Most often, a SCO molecule, being an octahedral metal complex with a  $d^4-d^7$  electron configuration, represents a transition between a low spin (LS, S = 0) and a high spin (HS, S = 2) state when the energy difference between the LS state and HS state is in the range of kT.<sup>7-9</sup> The process can be induced by an external stimulus such as temperature, pressure, and light irradiation.<sup>10-12</sup> Although many SCO complexes have been obtained in recent years, compounds with  $T_{1/2}$  in the range of room temperature or above are still rare.<sup>13-17</sup> So far it is still a great challenge to design and produce systems that can be tuned and exploited at room temperature.

In practice, Fe(II) complexes with six coordinating N atoms are most often used in SCO researches since they exhibit remarkably different magnetic properties and geometry structures between the HS and LS state.<sup>18</sup> The HS state usually exhibits a greater structural flexibility and structural distortion to ideal octahedral symmetry than the LS state. Therefore, in some Fe(II) complexes whose HS structures differ too much from that expected for LS state, the structural change required for SCO may be too large to be accommodated in a rigid solid lattice, then these complexes may tend to be trapped in their HS state and not undergo SCO on cooling.<sup>12</sup>

Among the Fe(II) systems, the family of  $[Fe(phen)_2(SCN)_2]$ (phen = 1,10-phenanthroline) molecule is one of the most thoroughly studied SCO complexes.<sup>19–23</sup> The influence of a substitution of the hydrogen atoms with electron-donating, electron-withdrawing, or bulky groups<sup>19</sup> and replacing the 4,7-CH group with N atoms has been investigated.<sup>21</sup> In 1999, a new kind of Fe(II) SCO complexes with the 5,6-substituted 1,10-phen derivative  $[Fe(dpp)_2(SCN)_2]$  py (dpp = dipyrido-[3,2-a:23'-c]phenazine; py = pyridine) was fabricated where the more extended aromatic ring is expected to show strong intermolecular  $\pi - \pi$  interactions to enhance the cooperativ-



ity.<sup>22,23</sup> However, to the best of our knowledge, no study has been reported so far on the ligands with 5,6-substituted imidazo-pyridine ring.

In this communication, we report the synthesis, structural determination, and magnetic properties of two isomorphous Fe(II) complexes  $FeL_2(SCN)_2$  [L1 = 2-(pyridin-3-yl)-1H-imidazo[4,5-f]1,10-phenanthroline (1); L2 = 2-(pyridin-4-yl)-1H-imidazo[4,5-f]1,10-phenanthroline (2)] with difference only in the position of one N atom in the pyridyl ring (Scheme 1). The single-crystal X-ray studies show that





complexes 1 and 2 crystallize in the same space group with similar  $\pi - \pi$  stacking mode. Magnetic measurements show that complex 1 exhibits a gradual full one-step SCO without hysteresis, centered at about 315 K, which is the highest SCO temperature among the family of  $[Fe(phen)_2(SCN)_2]$ .<sup>19–23</sup> However, with the bigger structural distortion in the coordination geometry, complex 2 is trapped in a stable HS state over the temperature range 10–300 K.

Ligands L1 and L2 are easily obtained in one step by reaction of 1,10-phenanthroline-5,6-dione with 3-pyridinecarboxaldehyde or 4-pyridinecarboxaldehyde according to the reported

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method.<sup>24</sup> Reaction of L1 or L2 with  $Fe(NO_3)_3 \cdot 9H_2O$  and KSCN in CH<sub>3</sub>CN using solvothermal method produces  $Fe(L1)_2(SCN)_2$  (1) and  $Fe(L2)_2(SCN)_2$  (2). Single crystals of 1 and 2 adopt the orthorhombic space group *Pbcn*, at both 100 K (LS state) and 420 K (HS state) for 1, and 100 K (HS state) for 2 (Table S1). The molecular structures of 1 and 2 at 100 K are shown in Figure 1. Selected bond lengths and angles



Figure 1. Molecular structure of (a) LS 1 and (b) 2.

for LS and HS states of 1 and 2 are listed in Table S2. 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 L1 ligands and two SCN anions. For 1 at 100 K, the Fe-N<sub>L1</sub> distances in the range of 1.970(3)-1.980(3) Å and Fe- $N_{SCN}$  bond lengths of 1.922(3) Å are typical for a LS Fe(II) ion (Table S2). At 420 K these coordination bond lengths increase by ca. 0.22 Å for Fe-N<sub>L1</sub> and ca. 0.15 Å for Fe-N<sub>SCN</sub> (Table S2), indicating a full spin transition as also observed by variabletemperature magnetic measurement. Complex 2 has a similar structure to 1. At 100 K, the Fe-N<sub>L2</sub> distances in the range of 2.216(2)-2.228(2) Å and Fe-N<sub>SCN</sub> bond lengths of 2.079(2) Å are typical for a HS Fe(II) ion (Table S2). Between the nearest  $[Fe(L)_2(SCN)_2]$  molecules there is a  $\pi - \pi$  stacking interaction connecting the ligands with an interplanar distance of 3.575 Å for LS 1, 3.671 Å for HS 1, and 3.545 Å for 2 (Figure S1), thus forming the 3D structure (Figure S2). The nearest Fe---Fe distance is 7.953 Å for LS 1, 8.105 Å for HS 1, and 8.138 Å for 2.

Moreover, the geometric constraints of the bidentate ligands result in a significant reduction of the N<sub>L</sub>-Fe-N<sub>L</sub> angles from 90° of an ideal octahedron [N2-Fe-N3 = 74.61(10)° for HS 1, 74.29(8)° for 2]. This distortion from  $O_h$  symmetry of the FeN<sub>6</sub> core is also found in the HS structure of similar [FeL<sub>2</sub>(SCN)<sub>2</sub>] (L = phen, bipyridine, dpp, or 1,4,5,8tetraazaphenanthrene) complexes.<sup>19,21,25</sup> The NCS groups are almost linear [177.2(4)° for HS 1; 178.7(3)° for 2], whereas the Fe-N-C(S) angles are bent [173.9(4)° for HS 1; 159.5(2)° for 2].

The magnetic property of complex 1 was investigated by solid state magnetic susceptibility measurements in the range of 10–390 K at a field of 5 kOe (Figure 2). The value of  $\chi_m T$  at 390 K is 3.53 cm<sup>3</sup> mol<sup>-1</sup> K, indicating that Fe(II) ion is in the



**Figure 2.**  $\chi_m T$  vs *T* plots for **1** ( $T_{1/2}$  = 315 K). The red plots recorded in the heating mode and the black plots recorded in the cooling mode. Inset: DSC data in the heating and cooling modes.

HS state. Upon cooling  $\chi_m T$  smoothly decreases until it reaches a value of 0.09 cm<sup>3</sup> mol<sup>-1</sup> K at 10 K, which highlights the spin transition of the Fe(II) ion centers from HS to LS state. The heating mode reveals that there is no thermal hysteresis loop, and the characteristic temperature  $T_{1/2} = 315$  K.

Variable-temperature magnetic susceptibility data for complex 2 were also collected with an applied dc field of 5 kOe in the 10–300 K temperature range (Figure S3). From 300 to 10 K, the values of  $\chi_m T$  in the range of 3.09–3.69 cm<sup>3</sup> mol<sup>-1</sup> K are typical values for a HS state Fe(II) ion. It indicates that 2 does not undergo SCO upon cooling and displays a stable HS state.

The octahedral distortion parameters  $\Sigma$  and  $\Theta$  have been calculated for the symmetry measures of the two FeN<sub>6</sub> cores.  $\Sigma$  is the sum of 190 –  $\alpha$ l for the 12 *cis*-N–Fe–N angles around the iron atom.  $\Theta$  is the sum of 160 –  $\theta$ l for the 24 unique projections of N–Fe–N angles to the triangular faces of the octahedron along its pseudo-3-fold axis.<sup>12,26,27</sup>  $\Sigma$  is a general measure of the deviation of a metal ion from an ideal octahedral, while  $\Theta$  represents the distortion of the MX<sub>6</sub> geometry from perfectly octahedral ( $O_h$ ) to trigonal prismatic ( $D_{3h}$ ). With fewer antibonding  $e_g^*$  electrons, the LS state always forms stronger metal–ligand bond and thus less deformable coordination sphere. Hence, the values of  $\Sigma$  and  $\Theta$  at LS state should be lower than that at HS state. A value of zero will indicate that the MX<sub>6</sub> group has perfect symmetry (e.g.,  $\Sigma = \Theta = 0$  indicates a perfect octahedron).

For 1 at LS state,  $\Sigma = 35$  and  $\Theta = 106$ , and the values increase respectively to  $\Sigma = 68$  and  $\Theta = 240$  upon LS to HS transition (Table 1). The values of  $\Theta$  agree with the reported

Table 1. Coordination Distortion Parameters for LS 1, HS 1, and 2

complex	$\Sigma$ (deg)	$\Theta$ (deg)
LS 1	35	106
HS 1	68	240
2	78	273

range of 107–164 for LS and 55–286 for HS in the FeL<sub>n</sub>(SCN)<sub>2</sub> complexes.<sup>26</sup> The corresponding  $\Delta\Sigma$  and  $\Delta\Theta$  values of respectively 33 and 134 thus reflect a distortion from  $O_h$  geometry, which are higher than that of the complex [Fe(phen)<sub>2</sub>(SCN)<sub>2</sub>] ( $\Delta\Theta = 100$ ;  $T_{1/2} = 176$  K). This observation disagrees with the literature, suggesting that the higher the  $\Delta\Theta$  value, the lower the  $T_{1/2}$  value.<sup>26</sup> This can be explained by that the way the local distortion of the coordination sphere is affected by its environment such as

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intra- and intermolecular interactions, which can play an important role regarding with cooperativity.<sup>28</sup>

For **2** with HS state,  $\Sigma = 78$  and  $\Theta = 273$ ; these values show greater structural distortions than a perfectly octahedral complex. Therefore, the HS structure of 2 differs more strongly from that expected for its LS form, which is why 2 does not undergo SCO upon cooling and displays a stable HS state.

From the crystal engineering aspect, there are some subtle differences in the H-bonds of the complexes. In LS 1 and HS 1 there exists the H-bond of N4A-H...S1. However, in complex 2, there is no H-bond (Figure S4). That may be the origin of the different coordination distortion parameters.

The differential scanning calorimetry (DSC) data (Figure 2 inset) show one exo- and one endothermic broad peak around 315 K in the heating and cooling mode, respectively, which agrees well with the spin transition. The thermogravimetric analysis (TGA) indicates that complex 1 is thermally stable up to about 400 °C (Figure S5).

In summary, two new mononuclear isomorphous Fe(II) complexes were synthesized and magnetically characterized. Although complexes 1 and 2 crystallize in the same space group with similar  $\pi - \pi$  stacking interaction, due to the different structural distortion in the coordination geometries, complex 1 exhibits thermally induced spin transition near room temperature ( $T_{1/2}$  = 315 K) without hysteresis, while 2 shows a stable HS state. Further detailed studies are in progress.

# ASSOCIATED CONTENT

### **Supporting Information**

X-ray crystallographic data in CIF format, synthetic details, materials and method, structural figures, PXRD, DSC and TGA plots, magnetic plots, crystallographic table, and tables containing bond distances and angles. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.5b00175.

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# Notes

The authors declare no competing financial interest.

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