

Assembling into Chiral Crystal of Spin Crossover Iron(II) Complex

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A new spin crossover iron(II) complex, $[\text{Fe}(\text{H}_2\text{L}^{2-\text{Me}})_2]\text{Cl}_2 \cdot 2\text{-PrOH} \cdot 0.5\text{H}_2\text{O}$ (**1**), has been prepared, where $\text{H}_2\text{L}^{2-\text{Me}} = (2\text{-methylimidazol-4-yl)methylidene}\text{histamine}$. The complex is a chiral molecule due to octahedral coordinations of two tridentate ligands, they are linked by the hydrogen bonds of $\text{NH} \cdots \text{Cl}^- \cdots \text{HN}$ through Cl^- ion into a chiral one-dimensional (1D) rod, and further the chiral rods with the same chirality are stacked to form a chiral crystal (conglomerate). The solvated sample showed a two-step SCO, and the desolvated sample showed an abrupt one-step SCO at $T_{1/2} = 180$ K.

The phenomenon of spin crossover (SCO) between high-spin (HS) and low-spin (LS) states has attracted much attention in the latest decade, because it has potential applications in switching and sensing devices.¹ In addition to temperature and pressure as external perturbation, spin-state transition induced by light, ultrashort laser, X-ray, and nuclear decay have been discovered.² Interesting SCO behaviors observed in the solid state, such as abrupt and multistep SCO, and hysteresis have been ascribed to cooperative effect between the SCO sites.¹ Coordination chemists have made considerable efforts toward synthesis of SCO complexes exhibiting cooperative effects and/or multifunctions.¹ Since it is expected that the link of chirality and magnetism introduces to materials several available magneto-optical properties,³ the introduction of chirality into SCO complexes would provide an interesting property. We have reported a family of SCO complexes with imidazole-containing ligands.⁴ In this study, we report a bulk-chiral iron(II) SCO complex, $[\text{Fe}(\text{H}_2\text{L}^{2-\text{Me}})_2]\text{Cl}_2 \cdot 2\text{-PrOH} \cdot 0.5\text{H}_2\text{O}$ (**1**) ($\text{H}_2\text{L}^{2-\text{Me}} = 2\text{-methylimidazol-4-yl)methylidene}\text{histamine}$).

A tridentate ligand $\text{H}_2\text{L}^{2-\text{Me}}$ was prepared by a 1:1 condensation reaction of histamine and 2-methyl-4-formylimidazole in ethanol. When a solution of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in 2-propanol was added to the ligand solution, orange rhombic crystals with the chemical formula $[\text{Fe}(\text{H}_2\text{L}^{2-\text{Me}})_2]\text{Cl}_2 \cdot 2\text{-PrOH} \cdot 0.5\text{H}_2\text{O}$ (**1**) were obtained.⁵ **1** showed a thermochromism from orange at room temperature to deep red at liquid nitrogen temperature.

1 crystallizes into an orthorhombic chiral space group $P2_12_12_1$ (No. 19).⁶ The crystal structure was determined at 296 K. The structure consists of one of two enantiomorphs $[\text{Fe}(\text{H}_2\text{L}^{2-\text{Me}})_2]^{2+}$, two Cl^- ions, and crystal solvents. An ORTEP drawing is shown in Figure 1. The Fe^{II} ion assumes an octahedral coordination environment with N_6 donor atoms of two tridentate ligands. The Fe–N bond distances are in the range of 2.134(4)–2.197(4) Å at 296 K, consistent with the values of the HS Fe^{II} state. The complex cation $[\text{Fe}(\text{H}_2\text{L}^{2-\text{Me}})_2]^{2+}$ has four imidazole NH sites at the terminal sites. All four imidazole groups are hydrogen-bonded to the Cl^- ions with the hydrogen-bond distances of $\text{N}(1) \cdots \text{Cl}(1) = 3.117(5)$ Å, $\text{N}(9) \cdots$

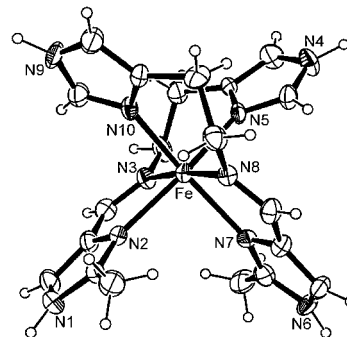


Figure 1. ORTEP drawing of $[\text{Fe}(\text{H}_2\text{L}^{2-\text{Me}})_2]^{2+}$. The Fe^{II} complex is a chiral molecule due to octahedral coordination of two tridentate ligands. All four imidazole groups are hydrogen-bonded to four Cl^- ions.

$\text{Cl}(2) = 3.179(4)$ Å, $\text{N}(4) \cdots \text{Cl}(1)^* = 3.167(5)$ Å, and $\text{N}(6) \cdots \text{Cl}(2)^* = 3.129(5)$ Å, where $\text{Cl}(1)^*$ and $\text{Cl}(2)^*$ (*: $-x + 1/2, -y + 1, z + 1/2$). By the hydrogen bonds, the two adjacent complexes $[\text{Fe}(\text{H}_2\text{L}^{2-\text{Me}})_2]^{2+}$ are doubly bridged by two Cl^- ions of $\text{Cl}(1)$ and $\text{Cl}(2)$ through the four hydrogen bonds of $\text{NH}(\text{formylimidazole residue}) \cdots \text{Cl}^- \cdots \text{HN}(\text{histamine residue})$ to form a rod-like 1D structure, as shown in Figure 2a. Within a rod, the Fe^{II} complexes with the same chirality are linked by the hydrogen bonds along the c axis to give a chiral rod. The adjacent 1D rods having the same chirality are stacked in a crystal lattice resulting in a chiral crystal (conglomerate), as shown in Figure 2b. The crystal solvents of 2-PrOH and H_2O are hydrogen-bonded to Cl^- ions and occupy the space between the 1D rods.

To confirm the conglomerate, circular dichroism (CD) spectra were measured and are shown in Figure 3. The enantiomeric CD spectra obtained from selected crystals provided definitive evidence that spontaneous resolution has occurred in the crystals.

Figure 4 shows the $\chi_{\text{M}}T$ vs. T plots. After the sample was quickly cooled from room temperature to 5 K, the $\chi_{\text{M}}T$ values were measured at a sweeping rate of 1 K min^{-1} from 5 to 350 K in the warming mode for the 1st run (\triangle), then from 350 to 5 K in the cooling mode for the 2nd run (∇), and finally from 5 to 350 K in the warming mode for the 3rd run (\blacktriangle). The elimination of the crystal solvents were determined by thermogravimetric analysis, and one 2-PrOH and 0.5 H_2O molecules of the crystal solvents ($2\text{-PrOH} \cdot 0.5\text{H}_2\text{O}$) were eliminated at less than 350 K. For the 1st run of the solvated sample, the $\chi_{\text{M}}T$ vs. T plots showed a frozen-in-effect and two-step SCO behavior. For the 2nd and 3rd runs of the desolvated sample, the $\chi_{\text{M}}T$ vs. T plots showed a reversible abrupt one-step SCO without hysteresis, where the inflection point was evaluated to be 180 K. The abrupt one-step SCO can be ascribed to intermolec-

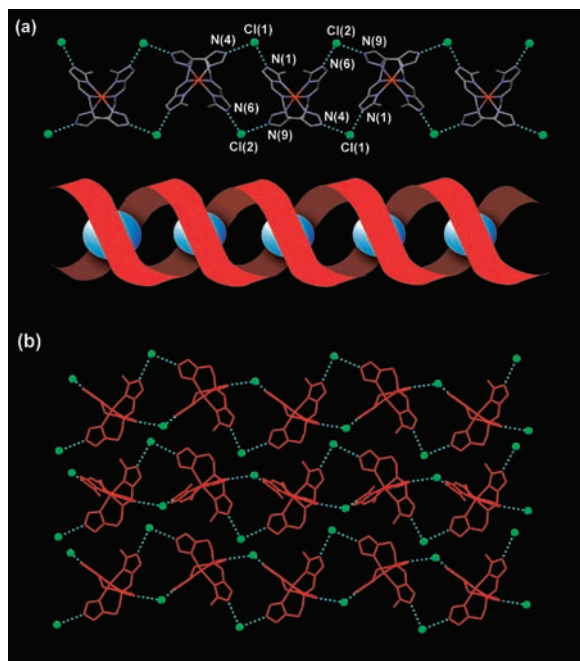


Figure 2. 1D chiral rod-like structure of $[\text{Fe}(\text{H}_2\text{L}^{2-\text{Me}})_2]\text{Cl}_2 \cdot 2\text{-PrOH} \cdot 0.5\text{H}_2\text{O}$ (**1**). (a) Two adjacent complex cations $[\text{Fe}(\text{H}_2\text{L}^{2-\text{Me}})_2]^{2+}$ are doubly bridged by two Cl^- ions ($\text{Cl}(1)$ and $\text{Cl}(2)$) through hydrogen bonds giving a chiral rod-like structure. (b) Adjacent rods with the same chirality are stacked to give a chiral crystal (conglomerate).

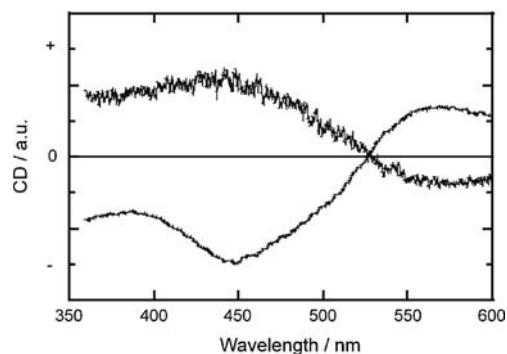


Figure 3. CD spectra of crystallites of **1** in KBr pellets. The two KBr pellets showed enantiomeric CD patterns.

ular interaction within a 1D rod. The difference of the SCO behaviors between the solvated and desolvated samples can be related to the spin-transition mechanism between the rods, since the solvents occupy the space between the rods.

In summary, we have reported a SCO Fe^{II} complex consisting of a chiral complex-cation $[\text{Fe}(\text{H}_2\text{L}^{2-\text{Me}})_2]^{2+}$, two Cl^- anions, and the crystal solvents. The complex cation $[\text{Fe}(\text{H}_2\text{L}^{2-\text{Me}})_2]^{2+}$ with four imidazole NH sites together with Cl^- ion forms a chiral 1D rod-like structure. The chiral 1D rod is constructed by hydrogen bonds of $\text{NH} \cdots \text{Cl}^- \cdots \text{NH}$, and further the rods with the same chirality are stacked to give a chiral crystal. The complex showed two-step and one-step SCO, depending on the crystal solvents existing between the rods. The correlation between the chiral crystal and SCO is now being studied.

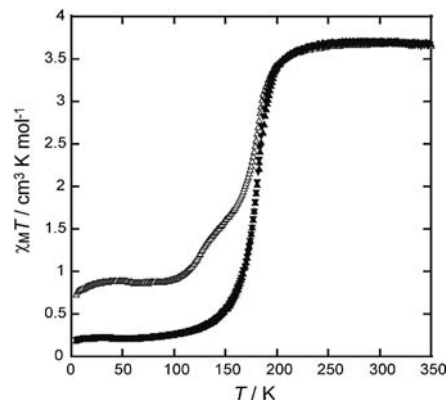


Figure 4. The $\chi_{\text{M}}T$ vs. T plots of $[\text{Fe}(\text{H}_2\text{L}^{2-\text{Me}})_2]\text{Cl}_2 \cdot 2\text{-PrOH} \cdot 0.5\text{H}_2\text{O}$ (**1**), showing two-step SCO for the solvated sample (1st run, \triangle) and an abrupt one-step SCO for the desolvated sample (2nd and 3rd run, ∇ and \blacktriangle).

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References and Notes

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- 5 Tridentate ligand $\text{H}_2\text{L}^{2-\text{Me}}$ was prepared by a 1:1 condensation of histamine (111 mg, 1 mmol) and 2-methyl-4-formylimidazole (110 mg, 1 mmol) in 10 mL of ethanol. A solution of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (94 mg, 0.5 mmol) in 10 mL of 2-propanol was added to the ligand solution (1 mmol). The mixed solution was allowed to stand overnight at room temperature, yielding orange colored crystals. Yield: 195 mg (32%). Anal. Calcd for $[\text{Fe}(\text{H}_2\text{L}^{2-\text{Me}})_2]\text{Cl}_2 \cdot 2\text{-PrOH} \cdot 0.5\text{H}_2\text{O} = \text{C}_{23}\text{H}_{35}\text{N}_{10}\text{O}_{1.5}\text{Cl}_2\text{Fe}$: C, 45.86; H, 5.86; N, 23.25%. Found: C, 45.71; H, 5.96; N, 23.33%.
- 6 X-ray crystallographic data for $[\text{Fe}(\text{H}_2\text{L}^{2-\text{Me}})_2]\text{Cl}_2 \cdot 2\text{-PrOH} \cdot 0.5\text{H}_2\text{O}$ at 296 K: formula $\text{C}_{23}\text{H}_{33}\text{N}_{10}\text{O}_2\text{Cl}_2\text{Fe}$, fw 608.33, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 9.130(2) \text{ \AA}$, $b = 16.536(4) \text{ \AA}$, $c = 19.866(4) \text{ \AA}$, $V = 2999.1(11) \text{ \AA}^3$, $Z = 4$, $D_{\text{calcd}} = 1.347 \text{ g/cm}^3$; $\mu = 7.184 \text{ mm}^{-1}$; $T = 296 \text{ K}$; $R = 0.0437$, $wR = 0.0593$, Flack parameter = 0.01(2). The crystallographic data can be obtained free of charge via Internet from the Cambridge Crystallographic Data Centre. Data (CCDC-703807).