Spin Crossover Iron(II) Complexes of (2-Methylimidazol-4-yl)methylideneamino-2-ethylpyridine: 2:1 $[Fe(HL^{Me})_2](PF_6)_2$ and 3:1 $[Fe(HL^{Me})_3](PF_6)_2$

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(2-Methylimidazol-4-yl)methylideneamino-2-ethylpyridine (HL^{Me}) functions as either bidentate or tridentate ligand to Fe^{II} ion to produce the 2:1 complex $[Fe(HL^{Me})_2](PF_6)_2$ (**1**) and the 3:1 complex $[Fe(HL^{Me})_3](PF_6)_2$ (**2**). Both complexes showed spin crossover (SCO) behaviors; **1** exhibited a gradual SCO between HS and (HS + LS)/2 and **2** showed an one-step abrupt SCO between HS and LS.

Spin crossover (SCO) between low-spin (LS) and high-spin (HS) states is one of the most spectacular and representative examples of molecular bistability,[1] and extensive studies have been carried out over the last two decades because of the potential application in information storage and visual display.[2] Interesting SCO properties with wide hysteresis loop or LIESST (light-induced excited spin state trapping) effect have been found for Fe^{II} complexes with a limited number of ligands like pyridine, pyrazole, and triazole derivatives.[1] In order to develop this important field, SCO complexes with new ligand systems must be developed. We have reported the metal complexes of multidentate ligands derived from the condensation reaction of 4-formylimidazole derivatives and various polyamines.[3] Of these, iron complexes have been found to be a new family of SCO with 1D and 2D extended network structures constructed by hydrogen bond NH···N, NH···Cl^-, or NH···π, and with the variety of SCO behaviors.[4] In this study, we focused on a ligand, (2-methylimidazol-4-yl)methylideneamino-2-ethylpyridine (see Chart 1, hereafter abbreviated as HL^{Me}) and synthesized two Fe^{II} SCO complexes with the different stoichiometry. The ligand plays as either bidentate or tridentate ligand depending on the synthetic condition to give the 2:1 complex $[Fe(HL^{Me})_2](PF_6)_2$ (**1**) and the 3:1 complex $[Fe(HL^{Me})_3](PF_6)_2$ (**2**). We report the syntheses, their SCO behaviors, and the crystal structures.

The 2:1 (**1**) and 3:1 (**2**) complexes were prepared by mixing the ligand, $FeCl_2\cdot4H_2O$, and KPF_6 with the 2:1:2 and 3:1:2 molar ratios.[5] The formulas of $[Fe(HL^{Me})_2](PF_6)_2$ and $[Fe(HL^{Me})_3](PF_6)_2$ were confirmed by the elemental analyses and the crystal structure analyses.[6] Both compounds showed thermochromism from yellow at ambient temperature to brown at liquid nitrogen temperature at the solid states.

Magnetic behavior of crystalline samples for **1** and **2** is shown in Figure 1, in the form of $\chi_M T$ vs T plots. The samples were quickly cooled from 300 to 5 K within a few seconds, and the $\chi_M T$ was measured upon warming from 5 to 300 K (▲, △) and then upon cooling from 300 to 5 K (▼, ▽) at the $1\,K\,min^{-1}$ sweeping mode under an applied magnetic field of 0.5 T. Figure 1 shows SCO behaviors of **1** and **2**. **1** exhibits a gradual SCO between HS and (HS + LS)/2. The $\chi_M T$ value of $3.5\,cm^3\,K\,mol^{-1}$ at 300–200 K is compatible with those of the reported HS Fe^{II} ($S = 2$) complexes. On cooling the sample temperature from 200 K, the $\chi_M T$ value decreases moderately from $3.4\,cm^3\,K\,mol^{-1}$ at 200 K to $1.9\,cm^3\,K\,mol^{-1}$ at 50 K. At 50 K, the $\chi_M T$ value is close to the value of 1:1 = HS:LS. The magnetic behavior of **1** also shows a frozen-in effect below 70 K, as seen in the difference of the $\chi_M T$ value vs T plots.

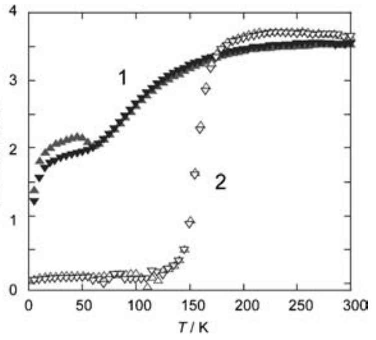

Figure 1. Magnetic behaviors of crystalline samples for **1** and **2**, in the form of $\chi_M T$ vs T plots.

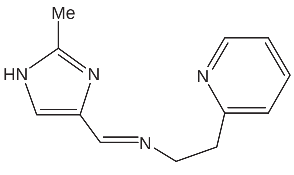

Chart 1.

2 shows a complete steep SCO between HS and LS states at $T_{1/2} = 155$ K without frozen-in effect and hysteresis. In the higher-temperature region of 300–180 K, the constant $\chi_M T$ value of $3.7\,cm^3\,K\,mol^{-1}$ is compatible with the reported HS Fe^{II} ($S = 2$) complexes. In the lower-temperature region of 140–5 K, a plateau value of nearly $0.0\,cm^3\,K\,mol^{-1}$ is compatible with the expected value for LS Fe^{II} ($S = 0$) complexes. In the region of 140–170 K, the $\chi_M T$ value changes steeply without hysteresis.

The temperature dependence of the Mössbauer spectra of **1** and **2** was investigated in the 4.2–298 K. For **1**, the spectra at 298, 200, and 150 K are similar and each spectrum consists of a doublet assignable to HS Fe^{II} species and impurity probably due to Fe^{III} species. Upon lowering the sample temperature from 150 K, relative intensity of the HS doublet decreases, while that due to LS Fe^{II} species increases. For example, at 40 K, the doublet due to HS species (isomer shift $\delta = 1.11\,mm\,s^{-1}$ and quadruple splitting $\Delta E_Q = 2.50\,mm\,s^{-1}$) and the doublet due to LS species ($\delta = 0.53\,mm\,s^{-1}$ and $\Delta E_Q = 0.48\,mm\,s^{-1}$) are observed. The Mössbauer results demonstrated that ca. 50% of Fe^{II} species converted from HS to LS state, being consistent with the result from the magnetic susceptibility.

The Mössbauer spectra of **2** are nearly the same in the warming and cooling modes, being consistent with no frozen-in effect. At 78 K in the LS state, the spectrum consists of a doublet assignable to LS Fe^{II} ($\delta = 0.50\,mm\,s^{-1}$ and $\Delta E_Q = 0.22\,mm\,s^{-1}$). At 298 and 200 K in the HS state, the spectrum consists of a doublet assignable to HS Fe^{II} species ($\delta = 1.07\,mm\,s^{-1}$ $\Delta E_Q = 1.10$

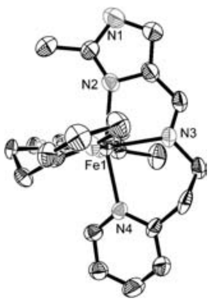

Figure 2. Molecular structure of **1** at 200 K. One of two Fe sites is shown.

$\mathrm{mm\,s^{-1}}$ at 200 K). At the SCO temperature region, the spectrum consists of two doublets assignable to the LS and HS $\mathrm{Fe^{II}}$ species (for example at 150 K, LS $\mathrm{Fe^{II}}$ ($\delta = 0.49\,\mathrm{mm\,s^{-1}}$, $\Delta E_\mathrm{Q} = 0.21\,\mathrm{mm\,s^{-1}}$) and HS $\mathrm{Fe^{II}}$ ($\delta = 1.04\,\mathrm{mm\,s^{-1}}$, $\Delta E_\mathrm{Q} = 1.45\,\mathrm{mm\,s^{-1}}$)).

The crystal structure of **1** consists of two crystallographically independent $\mathrm{Fe^{II}}$ molecules and four $\mathrm{PF_6}^-$ anions, where cations and anions showed no disorder. As seen in Figure 2, each $\mathrm{Fe^{II}}$ ion is octahedrally coordinated by $\mathrm{N_6}$ donor atoms of two tridentate ligands $\mathrm{HL^{Me}}$, in which an imidazole, an imine, and a pyridine nitrogen atoms per ligand participate into the coordination. The Fe(1)–N distances in the range of 2.166(5)–2.230(5) Å and the Fe(2)–N distances in the range of 2. 179(6)–2.214(5) Å are consistent with the values of the HS $\mathrm{Fe^{II}}$ complexes with the similar nitrogen donor atoms. There are no noteworthy intermolecular interactions to produce an extended structure in this complex.

The crystal structures of **2** were solved at 200 and 123 K, in order to reveal the structures in the HS and LS $\mathrm{Fe^{II}}$ states. The space group $C2/c$ does not change during the spin transition. The cation and anions showed no disorder. As shown in Figure 3a, $\mathrm{Fe^{II}}$ ion is octahedrally coordinated by $\mathrm{N_6}$ donor atoms of three bidentate ligands to give a chiral molecule (clockwise or anticlockwise molecule), in which an imidazole and imine nitrogen atoms per ligand participate into the coordination but pyridine nitrogen is free from coordination. The Fe–N distances at 200 K are in the range of 2.159(2)–2.246(3) Å, typical for HS $\mathrm{Fe^{II}}$ bound to $\mathrm{N_6}$ donors, and the Fe–N distances at 123 K are in the range of 1.990(2)–2.007(2) Å, typical for LS $\mathrm{Fe^{II}}$. The average Fe–N distance decreases from 2.189 Å at 200 K to 1.998 Å at 123 K by 0.19 Å, which is comparable with the value of the previously reported SCO complexes (ca. 0.2 Å). The N–Fe–N bond angles at 123 K are closer to a regular octahedron than those at 200 K. The crystal packing diagram of **2** is shown in Figure 3b. The most striking structural feature is 1D structure constructed by the intermolecular NH···N hydrogen bond between an imidazole group of a molecule and a pyridine nitrogen of the adjacent molecule, where the hydrogen-bond distance of N(1)···N(8) is 2.876(4) Å at 123 K. One of three imidazole groups per molecule participates into the construction of the 1D chain, and the remaining two imidazole groups are hydrogen bonded to the two $\mathrm{PF_6}^-$ ions. A steep SCO behavior can be attributed to the 1D chain.

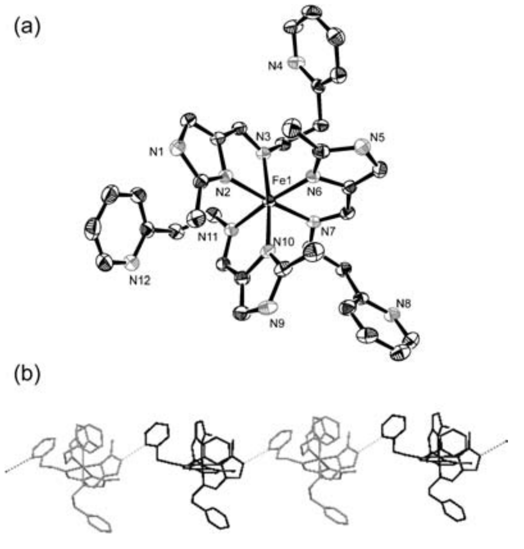

Figure 3. (a) Molecular structure of the cationic part of **2** at 123 K. (b) 1D structure constructed by the NH···N hydrogen bond between imidazole and pyridine.

In summary, a ligand, 2-methylimidazol-4-ylmethylideneamino-2-ethylpyridine, functions as either bidentate or tridentate ligand to $\mathrm{Fe^{II}}$ ion to produce the 2:1 and the 3:1 complexes, which are selectively synthesized by adjusting the molar ratio of $\mathrm{Fe^{II}}$ and ligand. These two complexes showed SCO behaviors with the extended structure, demonstrating that iron complexes of the ligand have fascinating features in giving a variety of structures and SCO behaviors.

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5 The syntheses of **1** and **2** were performed in the air, although the manipulation under inert atmosphere is recommended. A solution of 2-(2-aminoethyl)pyridine (0.245 g, 2 mmol) in 5 mL of methanol was added to a solution of 2-methyl-4-formylimidazole (0.221 g, 2 mmol) in 5 mL of methanol. The resulting solution was stirred on a hot plate at 50 °C for 15 min and then cooled to ambient temperature. To the ligand solution was added a solution of $\mathrm{Fe^{II}Cl_2\cdot 4H_2O}$ (0.193 g, 1 mmol) in 10 mL of methanol. To the mixture was added a solution of $\mathrm{KPF_6}$ (0.376 g, 2 mmol) in 20 mL of methanol. The resulting solution was stirred at room temperature for overnights. Yellow crystals were collected by suction filtration. Yield: 0.468 g (60%). Anal. Calcd for $\mathrm{[Fe(HL^{Me})_2](PF_6)_2\cdot H_2O}$: C, 36.38; H, 3.81; N, 14.14%. Found: C, 36.60; H, 3.67; N, 14.52%. IR(KBr): $\nu_\mathrm{C=N}$ 1606.2, 1634.7 $\mathrm{cm^{-1}}$. **2** was prepared similarly to **1** using 3 mmol of ligand solution, instead of 2 mmol of ligand solution. Yellow crystals. Yield: 0.35 g (35%). Anal. Calcd for $\mathrm{[Fe(HL^{Me})_3](PF_6)_2}$: C, 43.74; H, 4.28; N, 17.00%. Found: C, 42.99; H, 4.18; N, 16.67%. IR(KBr): $\nu_\mathrm{C=N}$ 1636.5 $\mathrm{cm^{-1}}$.

6 X-ray crystallographic data for **1** at 200 K: formula $\mathrm{C_{48}H_{60}Fe_2N_{16}O_2P_4F_{24}}$, fw 1584.66, monoclinic, $P2_1/n$ (No. 14), $a = 10.636(2)$, $b = 19.064(4)$, $c = 33.442(6)$ Å, $\beta = 93.651(7)^\circ$, $V = 6767(2)$ Å^3, $Z = 4$, $D_\mathrm{calcd} = 1.555\,\mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo\,K\alpha}) = 0.639\,\mathrm{mm^{-1}}$, $R = 0.083$, $R_w = 0.2244$. X-ray crystallographic data for **2** at 200 K: formula $\mathrm{C_{36}H_{42}FeN_{12}P_2F_{12}}$, fw 988.58, monoclinic, $C2/c$ (No. 15), $a = 37.408(7)$, $b = 11.474(3)$, $c = 22.196(4)$ Å, $\beta = 114.665(7)^\circ$, $V = 8657(2)$ Å^3, $Z = 8$, $D_\mathrm{calcd} = 1.517\,\mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo\,K\alpha}) = 0.517\,\mathrm{mm^{-1}}$, $R = 0.050$, $R_w = 0.146$.
X-ray crystallographic data for **2** at 123 K: formula $\mathrm{C_{36}H_{42}FeN_{12}P_2F_{12}}$, fw 988.58, monoclinic, $C2/c$ (No. 15), $a = 37.02(1)$, $b = 11.057(3)$, $c = 22.573(6)$ Å, $\beta = 116.075(9)^\circ$, $V = 8299(3)$ Å^3, $Z = 8$, $D_\mathrm{calcd} = 1.582\,\mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo\,K\alpha}) = 0.540\,\mathrm{mm^{-1}}$, $R = 0.052$, $R_w = 0.141$.