A Tripodal Ligand Containing Three Imidazole Groups Inducing Spin Crossover in Both Fe(II) and Fe(III) Complexes; Structures and Spin Crossover Behaviors of the Complexes

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A tripodal hexadentate ligand containing three imidazole groups gives spin-crossover iron complexes in both the +II and the +III oxidation states. The tetrafluoroborate salt of the Fe(II) complex shows a gradual spin transition in the temperature range 110–270 K. The corresponding Fe(III) complex shows a spin transition above 150 K, and at 300 K ca. 87% of the Fe(III) ion is in the high-spin state.

Spin-crossover (SCO) behavior between the low-spin (LS) and high-spin (HS) states has attracted increasing attention, because SCO is the most spectacular example of molecular bistability.[1] Bistable molecules can be used as molecular memories and switches in electronic devices.[2] The SCO phenomenon is observed in some octahedral $3d^4$–$3d^7$ metal complexes when the magnitude of the ligand field strength is comparable with the spin-pairing energy. SCO conditions depend on many factors, such as the kind and oxidation state of a metal ion, and the type of counter ion. An Fe(III) complex exerts a larger ligand-field strength than the corresponding Fe(II) complex, and therefore in general, one does not expect SCO behavior for both Fe(III) and Fe(II) complexes containing the same ligand. Here we report that the tetrafluoroborate salts of the Fe(II) and Fe(III) complexes with a tripodal ligand containing three imidazole groups, tris(2-{[(imidazole-4-yl)methylidene]amino}ethyl)amine = H₃L, show SCO behavior.
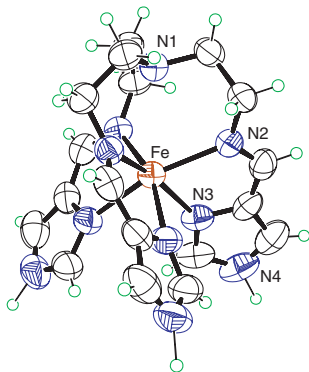

Figure 1. X-ray molecular structure of the cation of **1**.

Orange crystals of [Fe^{II}(H₃L)](BF₄)₂·3H₂O[3] (**1**) were isolated after the addition of NH₄BF₄ to a reaction mixture of FeCl₂·4H₂O, tris(2-aminoethyl)amine, and 4-formylimidazole (4-fim) in a 1:1:3 molar ratio in methanol. The corresponding dark red Fe(III) complex, [Fe^{III}(H₃L)](BF₄)₃·(4-fim)·H₂O[3] (**2**) was prepared by the same method as for **1** except that FeCl₃
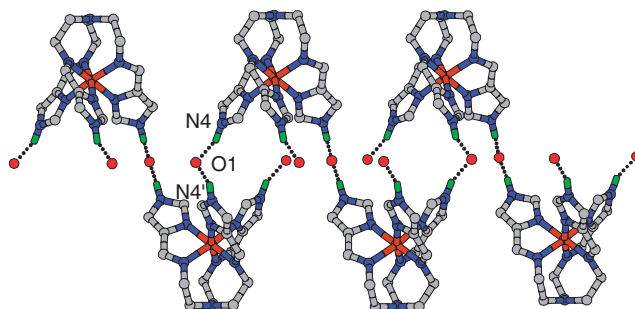

Figure 2. Crystal structure of **1** showing a puckered 2-D sheet structure (side view) formed by intermolecular hydrogen bonds through water molecules. Counter anions are omitted for clarity.
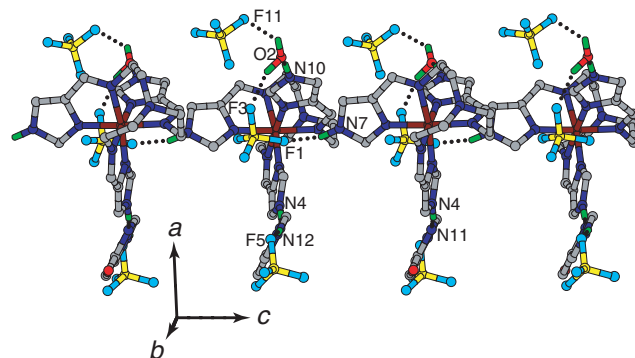

Figure 3. Crystal structure of **2** showing a comb-like structure at 93 K.

was used instead of FeCl₂·4H₂O, water being used as the solvent.

The X-ray structure of **1** was determined at 293 K and 108 K.[4] The Fe(II) ion is in a distorted octahedral environment and is coordinated by three imine nitrogen atoms and three imidazole nitrogen atoms (Figure 1). At 293 K, the average Fe–N bond distance is 2.192 Å, which is a typical value for a HS Fe(II) center. The two adjacent complex cations are connected in a tail-to-tail fashion by N–H···O(w)···H–N hydrogen bonds with the N···O distance of 2.790(9) Å and the N···O···N angle of 115.4(5)° to form a puckered 2-D sheet structure (Figure 2). The complex cation has a crystallographic three-fold axis. At 108 K, the average Fe–N bond distance is 1.985 Å, which is a typical value for a LS Fe(II) center, indicating SCO. No crystallographic phase transition was found. The X-ray structure of **2** was determined at 296 and 93 K.[5] Here again the space group was retained upon cooling. The molecular structure is similar

to that of **1**, and at 296 K the average Fe–N bond distance is 2.091 Å, which is a typical value for a HS Fe(III) center. The corresponding distance at 93 K is 1.967 Å, which is a typical value for the LS Fe(III)–N bond. The crystal has a comb-like structure (Figure 3). The complex cations are linked by intermolecular hydrogen bonds, N7–H···F1 (N7···F1 = 2.753(3) Å at 93 K), F3···H–O2 (F3···O2 = 2.750(3) Å), and O2···H–N10′ (O2···N10′ = 2.749(3) Å), to form a 1-D chain running along the c axis. The two hydrogen bonds, N4–H···N11 (N4···N11 = 2.808(4) Å) and N12–H···F5 (N12···F5 = 2.939(3) Å), contribute to form the teeth of a comb. A similar structure has been found in the perchlorate salt.[6]

The temperature dependence of the magnetic susceptibility of polycrystalline samples of **1** and **2** was investigated in the temperature range 5–300 K. The results are shown in Figure 4 in the form of $\chi_M T$ versus T plots. Complex **1** shows a gradual spin transition in the 110–270 K region. The $\chi_M T$ value of complex **2** in the 5–150 K temperature range is nearly constant at 0.58 cm³ K mol⁻¹, which indicates that Fe(III) is in the LS state in this temperature range. In the 150–300 K temperature range, the $\chi_M T$ value increases with increasing temperature from 0.60 cm³ K mol⁻¹ at 150 K to 3.88 cm³ K mol⁻¹ at 300 K. The $\chi_M T$ value at 300 K is lower than the spin-only value of 4.375 cm³ K mol⁻¹ for HS Fe(III) ($S = 5/2$, $g = 2.00$). This fact indicates that complex **2** is not completely in the HS state at 300 K but contains the LS species to some extent (ca. 13%).
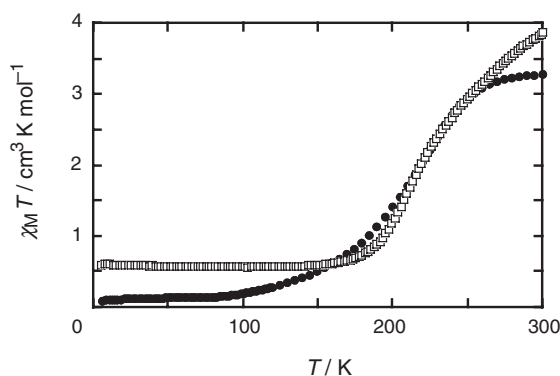

Figure 4. Magnetic behaviors of **1** (●), and **2** (□) in the form of $\chi_M T$ vs T plots.

The SCO behavior of **1** and **2** was also studied by ⁵⁷Fe Mössbauer spectroscopy. The spectra of **1** were measured at 78, 180, 220, and 298 K. At 78 K, the spectrum consisted of a unique doublet exhibiting quadrupole splitting ($\delta = 0.42$ mm s⁻¹, $\Delta E_Q = 0.20$ mm s⁻¹), demonstrating the existence of only the LS Fe(II) species.[7] At 180 and 220 K, another quadrupole doublet attributable to the HS Fe(II) species was observed (at 180 K, $\delta = 1.07$ mm s⁻¹, $\Delta E_Q = 1.92$ mm s⁻¹; at 220 K, $\delta = 1.06$ mm s⁻¹, $\Delta E_Q = 1.81$ mm s⁻¹). No signal due to the LS Fe(II) species was detected at 298 K. On the basis of deconvolution analyses of the spectra, it was shown that the mole fraction of the HS Fe(II) species increases with a rise in temperature: 0% (78 K), 23% (180 K), 44% (220 K), and 100% (298 K). The results agree with the magnetic susceptibility results. The Mössbauer spectra of **2** were measured at 78, 200, 240, and 298 K. At 78 K, the spectrum consisted of a unique doublet ($\delta = 0.17$ mm s⁻¹, $\Delta E_Q = 1.85$ mm s⁻¹), demonstrating the existence of only the

LS Fe(III) species. At 200 and 240 K, in addition to the LS Fe(III) doublet signal (at 200 K, $\delta = 0.14$ mm s⁻¹, $\Delta E_Q = 1.82$ mm s⁻¹; at 240 K, $\delta = 0.15$ mm s⁻¹, $\Delta E_Q = 1.80$ mm s⁻¹), a signal assignable to HS Fe(III) was observed (at 200 K, $\delta = 0.21$ mm s⁻¹, $\Delta E_Q \approx 0$ mm s⁻¹; at 240 K, $\delta = 0.26$ mm s⁻¹, $\Delta E_Q \approx 0$ mm s⁻¹). The mole fraction of the HS Fe(III) species increases with a rise in temperature: 0% (78 K), 16% (200 K), and 45% (240 K). These results agree well with the magnetic susceptibility results. At 298 K, the spectrum was extremely broadened. The averaged line shape will be observed when the rate of spin-state conversion between LS Fe(III) and HS Fe(III) is comparable with or faster than the time scale of the Mössbauer experiment (ca. 10^7 s⁻¹).[8]

In this report, we have shown the SCO behaviors of the Fe(II) and Fe(III) complexes containing the H₃L ligand. To the best of our knowledge, only one ligand (1,1′,4,4′,5,5′,6,6′-octahydro-2,2′-bipyrimidine) has been reported to generate SCO conditions in both Fe(II) and Fe(III) complexes, the structures of which have not been determined by X-ray crystallography.[9] We are currently conducting an extensive study of the family of SCO Fe(II), Fe(III), and mixed-valence Fe(II)–Fe(III)[10] complexes with the same tripodal ligand.

References and Notes
1   For example, J. A. Real, A. B. Gaspar, V. Niel, and M. C. Muñoz, *Coord. Chem. Rev.*, **236**, 121 (2003).
2   For example, M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, and T. Kawai, *Nature*, **420**, 759 (2002).
3   Satisfactory elemental analysis results (within ±0.3%) were obtained.
4   Crystallographic data for **1**: $T = 293$ K, formula weight 663.95, trigonal, space group $R32$ (No. 155), $a = 11.9901(5)$, $c = 35.553(2)$ Å, $V = 4426.4(6)$ Å³, $Z = 6$, $D_{calcd} = 1.497$ g·cm⁻³, μ(Mo Kα) = 6.01 cm⁻¹, 2272 unique reflections, R_1 ($I > 2\sigma(I)$) = 0.072, wR (all data) = 0.164. $T = 108$ K, formula weight 663.95, trigonal, space group $R32$ (No. 155), $a = 11.7867(6)$, $c = 33.967(2)$ Å, $V = 4086.7(3)$ Å³, $Z = 6$, $D_{calcd} = 1.619$ g·cm⁻³, μ(Mo Kα) = 6.50 cm⁻¹, 2100 unique reflections, R_1 ($I > 2\sigma(I)$) = 0.057, wR (all data) = 0.123.
5   Crystallographic data for **2**: $T = 296$ K, formula weight 810.82, monoclinic, space group $C2/c$ (No. 15), $a = 38.154(2)$, $b = 12.6320(4)$, $c = 14.1100(6)$ Å, $\beta = 95.892(1)°$, $V = 6764.6(5)$ Å³, $Z = 8$, $D_{calcd} = 1.592$ g·cm⁻³, μ(Mo Kα) = 5.55 cm⁻¹, 7620 unique reflections, R_1 ($I > 2\sigma(I)$) = 0.076, wR (all data) = 0.191. $T = 93$ K, formula weight 810.82, monoclinic, space group $C2/c$ (No. 15), $a = 37.619(4)$, $b = 12.1091(9)$, $c = 13.995(1)$ Å, $\beta = 92.480(2)°$, $V = 6368(1)$ Å³, $Z = 8$, $D_{calcd} = 1.691$ g·cm⁻³, μ(Mo Kα) = 5.90 cm⁻¹, 7205 unique reflections, R_1 ($I > 2\sigma(I)$) = 0.062, wR (all data) = 0.152. At 296 K, the LS species should exist to some extent, however, the presence of disorder was not indicated.
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8   Y. Maeda, N. Tsutsumi, and Y. Takashima, *Inorg. Chem.*, **23**, 2440 (1984).
9   M. G. Burnett, V. McKee, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, **1981**, 1492.
10 Y. Sunatsuki, Y. Ikuta, N. Matsumoto, H. Ohta, M. Kojima, S. Iijima, S. Hayami, Y. Maeda, S. Kaizaki, F. Dahan, and J.-P. Tuchagues, *Angew. Chem., Int. Ed. Engl.*, **42**, 1614 (2003).