# An Abrupt Spin Crossover $Fe^{II}$ Complex Based on Homochiral Chain

Nicolas Bréfuel, Sergiu Shova,[†] Jean-Pierre Tuchagues,[††] and Naohide Matsumoto[*]
*Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555*
[†]*Institute of Applied Physics, Academy of Sciences of Moldova, Academiei str. 3. 2028 Chisinau, Moldova*
[††]*Laboratoire de Chimie de Coordination du CNRS, UPR 8241, 205 route de Narbonne, 31077 Toulouse, France*

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A new $Fe^{II}$ complex with a linear hexadentate ligand involving one terminal imidazole and one terminal imidazolato moiety, $[FeHL^{2\text{-}Me}]ClO_4$, has been synthesized, where $H_2L^{2\text{-}Me}$ denotes [bis(2-methyl-4-formylimidazolidene)aminopropyl]ethylenediamine. This complex shows an abrupt spin-crossover at $T_{1/2} = 165.5$ K and assumes a homochiral 1D chain structure through hydrogen bonds between the imidazole and imidazolato groups of adjacent molecules.

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High-spin (HS, $^5T_2$) ↔ low-spin (LS, $^1A_1$) crossover in $Fe^{II}$ complexes has been extensively studied over the last two decades.[1] While the spin-crossover (SCO) behavior is a single molecule property, the interactions between SCO sites are the key to control such SCO properties as steepness, width of the hysteresis loop or LIESST (light-induced excited spin state trapping) effect.[2] Monitoring these parameters is required for potential technological applications such as information storage or visual display.[3] From this viewpoint, the synthesis of SCO complexes exhibiting interactions between metal centers is of current interest. Along this line, polymeric SCO systems in which metal centers are linked through bridging ligands, affording strong intermolecular interactions, have been extensively investigated.[4] Another strategy is based on the supramolecular approach where the SCO sites are connected by hydrogen bonds or $\pi$–$\pi$ stacking interactions.[5] Previously, we have reported a new family of SCO complexes with tripodal ligands involving three imidazole groups: $[Fe^{II}H_3L^R][Fe^{II}L^R]X$[6] and $[Fe^{II}H_3L^R][Fe^{III}L^R]X_2$[7] complexes show abrupt and multi-step SCO behaviors, their two-component $Fe^{II}/Fe^{III}$ sites being connected through imidazole–imidazolato hydrogen bonds into extended 2D network structures.

In this study, we designed a new 1D $Fe^{II}$ complex with the hexadentate linear ligand derived from the 1:2 Schiff base condensation of *N*,*N*′-bis(3-aminopropyl)ethylenediamine and 2-methyl-4-formylimidazole. The monodeprotonated species, $[Fe^{II}HL^{2\text{-}Me}]^+$, involving an imidazole and an imidazolate moieties, can function as a self-complementary building block to form 1D structure. We report here the abrupt SCO behavior and the crystal structures of the LS and HS states.

The crystals of $[FeHL^{2\text{-}Me}]ClO_4$ show thermochromism from orange at room temperature to dark red at liquid nitrogen temperature, suggesting SCO.[8] The magnetic susceptibility of a microcrystalline sample has been measured in the temperature range 5–300 K at 1 K min$^{-1}$ sweeping rate: first the sample was quickly cooled down from room temperature to 5 K, then the heating and cooling modes were successively run (Figure 1). At 5 K, the value of the $\chi_M T$ product (0.07 cm$^3$ mol$^{-1}$ K) corresponds to the LS state. Upon heating, an abrupt increase of $\chi_M T$ product is observed in the 140–190 K range: the SCO temperature, $T_{1/2} = 165.5$ K, has been evaluated from the first derivative of $\chi_M T$. Above 190 K, the $\chi_M T$ product reaches a plateau at ca. 3.5 cm$^3$ mol$^{-1}$ K, indicating a complete crossover to the $Fe^{II}$ HS state.

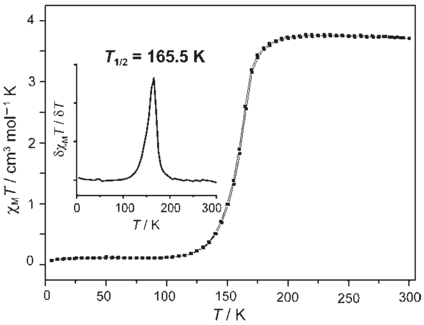

**Figure 1.** Thermal variation of the $\chi_M T$ product of $[Fe^{II}HL^{2\text{-}Me}]ClO_4$.

Upon cooling down the system, the $\chi_M T$ product shows the same variation as in the warming mode (except for small differences in the SCO temperature range): hysteresis and frozen-in effects are not observed, despite the interactions between adjacent molecules through the imidazole–imidazolate hydrogen bonds present in this material (vide infra).

Mössbauer spectra have been recorded in the 80–230 K temperature range (Figure 2). The SCO is observed over a 40 K temperature range, between ca. 140 and 190 K, in agreement with the magnetic data.

The quadrupole splitting of the LS doublet is very small ($\Delta Eq_{LS} = 0.103$ mm s$^{-1}$ at 80 K) indicating a very weak distortion of the octahedral symmetry around the $Fe^{II}$ ion for this spin state, in accordance with the crystallographic data (vide infra). $\Delta Eq_{HS}$ parameters are in the range of values observed in literature for HS complexes including $Fe^{II}N_6$ core.

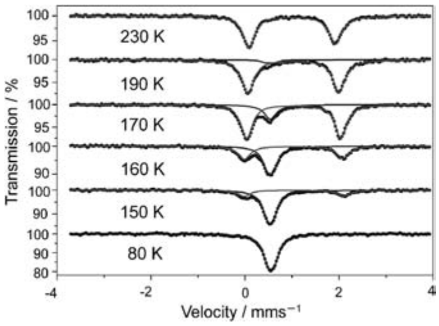

**Figure 2.** Selected Mössbauer spectra of $[Fe^{II}HL^{2\text{-}Me}]ClO_4$. The solid lines represent the fitted curves.

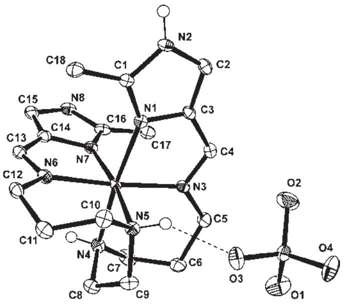

**Figure 3.** X-ray molecular structure of $[Fe^{II}HL^{2\text{-}Me}]ClO_4$ at 100 K. (hydrogen bond: $N(5)\cdots O(3) = 2.932$ Å).

The molecular structure has been investigated by single crystal X-ray technique at 100 K (LS) and 180 K (HS).[9] Figure 3 illustrates how the hexadentate Schiff base ligand wraps the metal center with the six nitrogen donor atoms ($N_6$) in a slightly distorted octahedral geometry and shows the hydrogen bond between the complex cation and the perchlorate counter anion. Though the ligand is achiral, the resulting $Fe^{II}$ complex is a chiral molecule due to the possible clockwise ($\Delta$) or anticlockwise ($\Lambda$) wrapping of the ligand about the metal.

The same space group, *Pbca*, is retained during the HS → LS transition while the unit cell decreases from 4434 $Å^3$ to 4253 $Å^3$ by 4.1%, being compatible with the values reported for $FeN_6$ core SCO complexes.[10] The spin state can be identified for each temperature: at 180 K, the Fe–N distances ($d_{Fe\text{–}N} =$ 2.134(3)–2.212(3) Å) are characteristic of a HS configuration while the corresponding values at 100 K ($d_{Fe\text{–}N} =$ 1.990(2)–2.027(2) Å) evidence a LS complex. In the same way, the N–Fe–N bond angles at 100 K are closer to the values of the regular octahedron, in agreement with a less-distorted geometry associated with the LS state.

Adjacent molecules are connected by $NH\cdots N^-$ hydrogen bonds between their imidazole and imidazolate groups to give a homochiral chain, as shown in Figure 4.

The adjacent homochiral zig-zag chains with the different chiralities are alternately arrayed to give achiral crystal, as found for a $Cu^{II}$ complex with a similar pentadentate Schiff base ligand.[11]

This study demonstrates how the $[Fe^{II}HL^{2\text{-}Me}]ClO_4$ complex, containing both imidazole and imidazolate moieties in one molecule, acts as a self-complementary unit to build an extended chain structure and to yield a abrupt SCO. Extensive work is in progress to design new compounds of this family to generate hysteretic behaviors associated to bulk chirality of the SCO material.

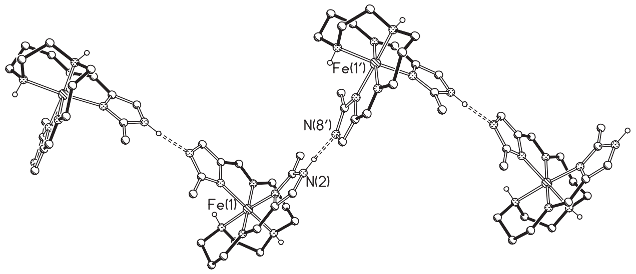

**Figure 4.** View of the extended 1D structure through imidazole–imidazolate hydrogen bond of $[Fe^{II}HL^{2\text{-}Me}]ClO_4$.

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## References and Notes

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8 $H_2L^{2\text{-}Me}$ ligand was prepared by 1:2 condensation reaction of *N*,*N*′-bis(3-aminopropyl)ethylenediamine and 2-methyl-4-formylimidazole in methanol. To the pale yellow solution of the ligand was added a solution of sodium methoxide (1 equiv.) in methanol. Then a solution of $Fe^{II}(ClO_4)_2\cdot 6H_2O$ (1 equiv.) in methanol was added dropwise to the resulting methanolic solution. Because of the air sensitivity of $Fe^{II}$ species, the synthesis of the complex has been carried out under nitrogen atmosphere (afforded by glove box or schlenk techniques). Slow crystallization gave orange crystals stable in the open atmosphere (yield = 70%). Anal. Calcd for $FeC_{18}H_{29}N_8ClO_4$: C, 42.16; H, 5.87; N, 21.85%. Found: C, 41.76; H, 5.57; N, 21.61%.

9 X-ray crystallographic data for $[Fe^{II}HL^{2\text{-}Me}]ClO_4$: at 180 K: formula = $C_{18}H_{29}N_8ClO_4Fe$, fw 512.79, orthorhombic, space group *Pbca* (No. 61), $a = 13.306(3)$, $b = 15.655(3)$, $c = 21.288(4)$ Å, $V = 4434.4(15)$ $Å^3$, $Z = 8$, $D_{calcd} = 1.536\ g\,cm^{-3}$, $R_{int} = 0.0447$, $R_1 = 0.0983$, $wR_2 = 0.0869$, GOF = 0.997; X-ray crystallographic data at 100 K: orthorombic, space group *Pbca* (No. 61), $a = 12.734(3)$, $b = 15.289(3)$, $c = 21.844(4)$ Å, $V = 4253.0(15)$ $Å^3$, $Z = 8$, $D_{calcd} = 1.602\ g\,cm^{-3}$, $R_{int} = 0.0593$, $R_1 = 0.1188$, $wR_2 = 0.1132$, GOF = 1.010.

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