Inorg. Chem. **2006**, *45*, 10019–10021

Inorganic Chemistry

Communication

Spin Transition in a Chainlike Supramolecular Iron(II) Complex

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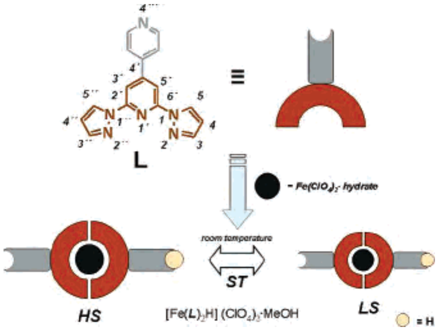
Received July 4, 2006

A one-dimensional supramolecular head-to-tail N^+–H···N-type hydrogen-bonded chain of the complex $[Fe^{II}(\mathbf{L})_2H](ClO_4)_3\cdot MeOH$ [**L** = 4′-(4‴-pyridyl)-1,2′:6′1″-bis(pyrazolyl)pyridine] exhibits a reversible, thermally driven spin transition at 286 K with a hysteresis loop of ca. 2 K.

Among the group of magnetic phenomena, the spin transition (ST) of six-coordinate iron(II) compounds has been receiving broad attention because of its diverse change in physical properties (magnetism, color, structure, etc.). This change can be triggered by applying external parameters such as temperature, pressure, and light intensity to the macroscopic samples.[1] It has been well recognized that a change of the Fe−ligand bond distances by ca. 0.2 Å plays a key role in transmitting the elastic interaction between the ST sites in the solid state, leading ultimately to cooperative effects. Hence, the spin-state conversion can be accompanied by hysteresis effects, exhibiting the extent of cooperativity in the crystal lattice.[1a] Supramolecular approaches (coordination polymers, hydrogen bonding, π−π stacking, etc.) were recently applied to molecular ST modules, partially with the objective to increase the ST temperatures and the magnitude of cooperativity.[2−4]

Scheme 1. Schematic Representation of the Synthesis of ST Complex **1**



Herein, we report on the synthesis, structure, and magnetic and Mössbauer characterization of the ST complex $[Fe^{II}(\mathbf{L})_2H](ClO_4)_3\cdot MeOH$ [**L** = 4′-(4‴-pyridyl)-1,2′:6′1″-bis(pyrazolyl)pyridine] (**1**). Compound **1** was synthesized from 1 equiv of $Fe^{II}(ClO_4)_2$ hydrate and 2 equiv of ligand **L**, giving a red precipitate in 84% yield (Scheme 1).[5] Recrystallization was carried out in MeOH, and the obtained red crystals were used for X-ray and magnetic studies. The detailed synthesis of ligand **L** is given in the Supporting Information.

Single-crystal X-ray diffraction studies of **1** reveal the monoclinic space group $P2_1/c$ (Figure 1).[6] Exactly one

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(5) When iron(II) perchlorate hydrate (76 mg, 210 μmol) in MeOH (50 mL) was added to the CH_2Cl_2 solution (120 mL) of ligand **L** (121 mg, 420 μmol) with constant stirring at 25 °C, an immediate red precipitate resulted. The red precipitate was filtered out and washed with MeOH and CH_2Cl_2 to afford complex **1**. The product was crystallized in MeOH for 7 days to get dark-red crystals. Anal. Calcd (found) for $C_{33}H_{29}N_{12}O_{13}Cl_{13}Fe$: C, 41.12 (41.76); H, 3.03 (3.05); N, 17.44 (18.46).

10.1021/ic0612350 CCC: $33.50

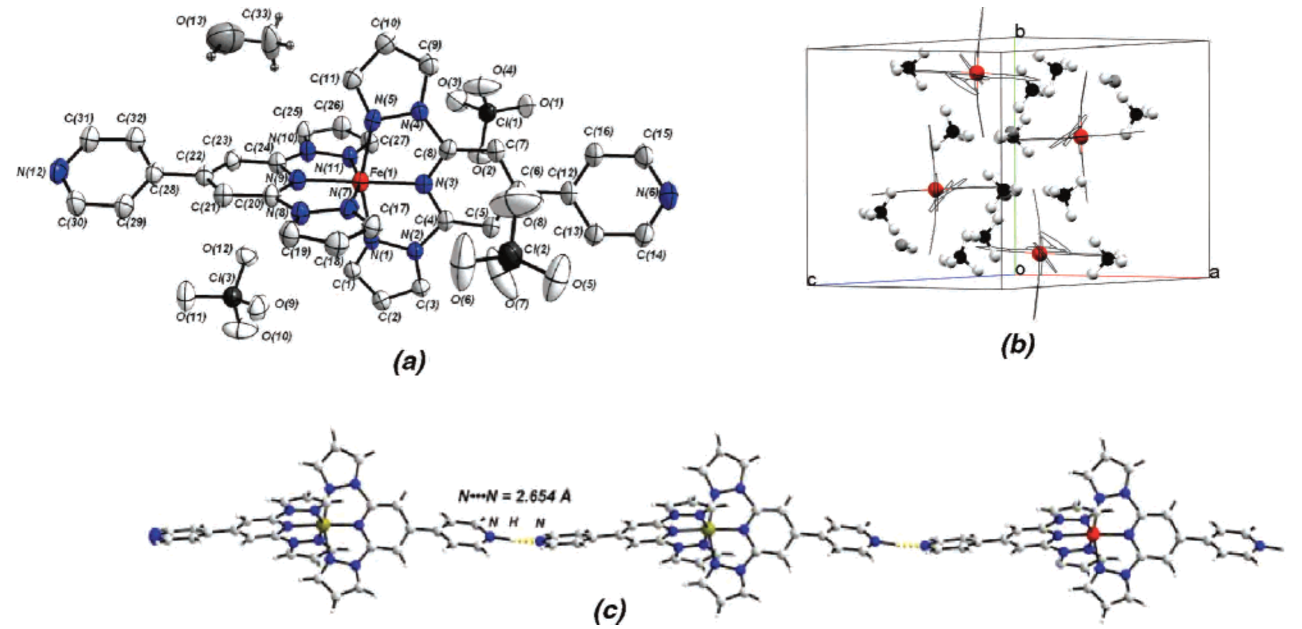

Figure 1. (a) ORTEP view of a complex **1** (30% probability ellipsoids) unit measured at 180 K. Selected bond lengths (Å): Fe−N(1) = 1.968(6), Fe−N(3) = 1.891(5), Fe−N(5) = 1.962(6), Fe−N(7) = 1.946(5), Fe−N(9) = 1.883(5), Fe−N(11) = 1.961(5). Selected bond angles (deg): N(9)−Fe(1)−N(3) = 174.91(2), N(9)−Fe(1)−N(7) = 80.4(2), N(3)−Fe(1)−N(7) = 94.7(2), N(9)−Fe(1)−N(11) = 80.3(2), N(3)−Fe(1)−N(11) = 104.5(2), N(7)−Fe(1)−N(11) = 160.8(2), N(9)−Fe(1)−N(5) = 98.9(2), N(3)−Fe(1)−N(5) = 79.8(2), N(7)−Fe(1)−N(5) = 93.2(2), N(11)−Fe(1)−N(5) = 89.2(2), N(9)−Fe(1)−N(1) = 101.7(2), N(3)−Fe(1)−N(1) = 79.8(2), N(7)−Fe(1)−N(1) = 92.4(2), N(11)−Fe(1)−N(1) = 92.1(2), N(5)−Fe(1)−N(1) = 159.2(2). Hydrogen atoms other than MeOH are omitted for clarity. (b) Molecular packing of the complex. (c) Supramolecular 1D N^+−H···N-type hydrogen-bonded chain structure of the complex. The counter ions are omitted for clarity.

MeOH solvent molecule per molecule of complex **1** is included in the crystal lattice. One of the 4′-substituted pyridyl groups of the complexed ligand **L** is protonated.

The resulting pyridinium cation forms a N^+−H···N-type hydrogen bond to the unprotonated 4′-substituted pyridine of the neighboring complex (N···N distance = 2.654 Å). Thus, the presence of hydrogen-bonded pyridinium cations (which are counterbalanced by additional perchlorate anions) is responsible for the formation of an infinite one-dimensional (1D) chain. The C(15)−N(6)−C(14) bond angle (120.40°) in the pyridinium unit is widened in comparison with the respective angle of the unprotonated pyridine unit (118.45°).[7] At 180 K, the coordination environment of the iron(II) metal ion can be described as a distorted octahedron. The Fe−N distances vary from 1.883(5) to 1.968(6) Å, indicating the presence of an iron(II) low-spin (LS) state. Temperature-dependent single-crystal X-ray studies show an increase in the unit cell volume from 3875 Å^3 at 180 K to 4012 Å^3 at 350 K without any change of the space group (see the Supporting Information). This volume change is a first evidence that thermal ST takes place in **1**.

The ST behavior was also confirmed by the bulk magnetic measurements of a polycrystalline sample of **1** in the temperature range of 4.5−380 K (Figure 2). At 380 K, the product of molar magnetic susceptibility and temperature, $\chi_M T$, is 3.71 emu·K/mol, which is close to the expected value for a high-spin (HS; $S = 2$) state iron(II) ion. Upon cooling, $\chi_M T$ abruptly decreases to a value of 0.28 emu·K/mol at 200 K and reaches a minimum value of ca. 0.14 emu·K/mol at 4.5 K. The latter value can be attributed to the iron(II) LS ($S = 0$) state. However, a residual magnetic moment of ca. 0.14 emu·K/mol indicates the presence of a trace paramagnetic impurity. Measurements performed in both heating (↑) and cooling (↓) cycles have revealed the occurrence of a ca. 2 K wide thermal hysteresis loop ($T_{1/2}$↑ = 287 K and $T_{1/2}$↓ = 285 K). Notably, the ST temperature is almost close to room temperature with a $T_{1/2}$ of 286 K. The presence of a thermal hysteresis loop clearly demonstrates the existence of a significant level of cooperativity in the solid state. At this point, the origin of cooperativity in **1** is not clear; it is probably mediated by the hydrogen bonds and/or the trapped

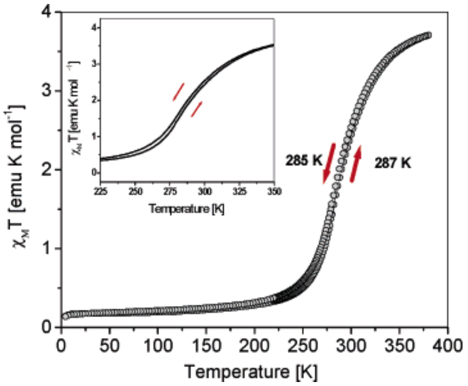

Figure 2. $\chi_M T$ vs T plot for the polycrystalline complex **1** from 4.5 to 380 K (↓ cooling mode and ↑ heating mode) with a 1000-Oe applied dc magnetic field. The inset shows the hysteresis loop ($\Delta T_{1/2} \sim 2$ K).

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(6) Crystal data for **1**: $C_{33}H_{29}N_{12}O_{13}Cl_3Fe$; monoclinic; space group $P2_1/c$; fw = 963.88; a = 13.537(3) Å; b = 15.127(3) Å; c = 19.890(4) Å; β = 107.89(3)°; V = 3875.8(13) Å^3; crystal size = 0.44 × 0.10 × 0.08 mm^3; index ranges = $16 \le h \le 16$, $-18 \le k \le 16$, $-24 \le l \le 17$; θ range for data collection = 1.58−25.75°; Z = 4; D_{obsd} = 1.652 mg/cm^3; F(000) = 1968; μ = 0.679 mm^{-1}; $R(F_o)$ = 0.0837; $R_w(F)$ = 0.2114; GOF on F^2 = 0.980; T = 180(2) K.

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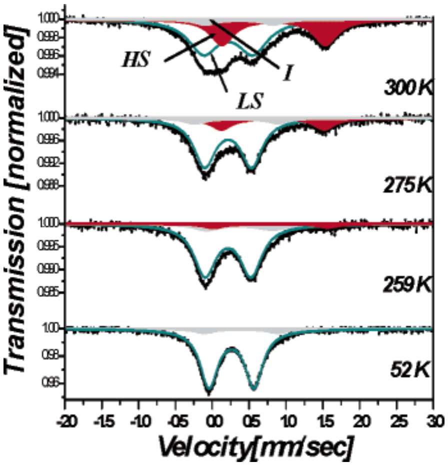

Figure 3. Zero-field ^{57}Fe Mössbauer spectra of **1** (dotted lines) and their least-squares best fits.

Table 1. Mössbauer Data for Complex **1** at Different Temperatures[a]

T [K]	component	δ_{iso} [mm/s]	ΔE_Q [mm/s]	Γ [mm/s]	AR [%]
300	LS	0.33(1)	0.67(2)	0.49(2)	58
	HS	0.947(4)	1.403(9)	0.38(2)	35
	I	0.37(5)	0.9(1)	0.35	7
275	LS	0.33(1)	0.64(1)	0.35(2)	76
	HS	0.94(2)	1.40(2)	0.33(4)	17
	I	0.44(4)	1.1(1)	0.36(9)	7
259	LS	0.33(1)	0.63(3)	0.36(2)	83
	HS	0.91(7)	1.5(2)	0.30(9)	11
	I	0.48(5)	0.9(2)	0.4(1)	6
52	LS	0.373(2)	0.608(2)	0.288(5)	93
	I	0.49(3)	0.98(6)	0.31(8)	7

[a] δ_{iso} = isomer shift relative to α-Fe, ΔE_Q = quadrupole splitting, Γ = width of the line, and AR = area ratio of the components A_{HS}/A_{tot}. Statistical standard deviations are in parentheses.

MeOH molecules. Noticeably, $T_{1/2}$ of complex **1** is 26 K higher than that of the unsubstituted 2,6-bis(pyrazol-1-yl)-pyridineiron(II) complex.[8]

The zero-field ^{57}Fe Mössbauer spectra for a powdered sample of complex **1** are displayed in Figure 3, and the spectroscopic data obtained by the least-squares fitting of the experimental spectra are given in Table 1. The spectra were collected in the warming and cooling modes without any discernible differences. A closer look at the spectra measured at 300, 275, 259, and 52 K reveals an asymmetric line splitting with a visible shoulder. Least-squares analysis of the spectra have shown the presence of a mixture of HS and LS states at 300 K. The parameters of the main doublet [58%; $\Delta E_Q = 0.67(2)$ mm/s, $\delta_{iso} = 0.33(1)$ mm/s] point to the presence of LS state iron(II). The second doublet (35%) parameters [$\Delta E_Q = 1.403(9)$ mm/s, $\delta_{iso} = 0.947(4)$ mm/s] are typical for a HS state iron(II) (Table 1). At 300 and 275 K, the molar fractions of the LS and HS states determined from the Mössbauer spectra and from the magnetic susceptibility data differ noticeably. This difference is due to the larger Lamb−Mössbauer factor for the molecules in the LS state than in the HS state.[9] Upon cooling down to 275 and 259 K, the LS fraction has further increased to 76% and 83%, respectively, at the expense of the HS state iron(II) fraction. At a temperature of 52 K, the spectrum [$\Delta E_Q = 0.608(2)$ mm/s, $\delta_{iso} = 0.373(2)$ mm/s] corresponds only to a 93% LS state fraction exclusive of any HS state iron(II) component, which is consistent with the magnetic susceptibilty data. Furthermore, the spectra at 300−52 K reveal the presence of a 7% additional component (I). This 7% spin state might be attributed to the presence of a slightly changed coordination environment at the chain ends of **1** or HS ferric impurities.[10] Overall, these results fully confirm the complete transition of the HS state into the LS state at 52 K.

In summary, we have succesfully designed and synthesized a ST building block [Fe^{II}(**L**)$_2$H](ClO$_4$)$_3$·MeOH, which forms a 1D N$^+$−H···N-type hydrogen-bonded chainlike structure. Importantly, the complex displays reversible ST from the HS ↔ LS state around room temperature with a ca. 2 K wide hysteresis loop. Variable-temperature single-crystal X-ray studies show a sweeping increase in the unit cell volume of about 3.5%. Furthermore, Mössbauer investigations of **1** validate the complete spin-state conversion (HS to LS) at 52 K. Complex **1**, which has been shown to exhibit a ST with thermal hysteresis around room temperature, represents an interesting building block in supramolecular self-assembly. The construction of higher dimensional architectures exploiting this ST module is under investigation.

Acknowledgment. The authors thank the European Science Foundation (FunSMARTs Project) and the EC-FP VII STREP BIOMACH (Grant MMPN-CT-2003-505-487) for financial support. They extend their special thanks to Prof. H. Hahn for providing the instrument facilities.

Supporting Information Available: Experimental details, synthesis of ligand **L**, and X-ray crystallographic parameters (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC0612350

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