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Spin crossover in two 1D Fe(II) polymers with 1,2,4-triazole thiourea building blocks

Houria Benaissa[1] · Aurelian Rotaru[2] · Yann Garcia[1]

Abstract

The 1D chain [Fe(Etutrz)$_3$](ClO$_4$)$_2$·1.5H$_2$O (**2**) (Etutrz = 1-ethyl-3-(4H-1,2,4-triazol-4-yl) thiourea), displays pronounced thermochromism with a purple color at 77 K while the sample is white at 300 K. Investigation of magnetic properties reveal an abrupt spin transition around 227 K. Differential scanning calorimetry studies on cooling display a first order phase transition at around 200 K with an entropy variation of $\Delta S = 61.3$ J mol^{-1} K^{-1}. ^{57}Fe Mössbauer spectroscopy of **2** confirms a complete spin transition with a 100% high-spin population at 300 K (isomer shift $\delta^{HS} = 1.04(1)$ mm/s, quadrupole splitting $\Delta E_Q = 2.86(2)$ mm/s). The Fe(II) ions convert to the low-spin state at 78K ($\delta^{LS} = 0.53(2)$ mm/s). The quadrupole splitting, $\Delta E_Q = 0.29(2)$ mm/s, confirms the presence of distorted octahedra within the 1D chain. The 1D chain [Fe(Etutrz)$_3$](BF$_4$)$_2$·2MeOH (**1**) exhibits a different magnetic behavior with a gradual spin conversion at $T_{1/2} = 221$ K, whereas thermochromic properties are maintained.

Keywords ^{57}Fe Mossbauer spectroscopy · Coordination polymers · Spin crossover · 1D chains · Sensors

1 Introduction

Spin crossover (SCO) molecular switches are currently considered as potential components of memory devices, displays, thermal and pressure sensors [1, 2]. As the development of such materials continues to grow [3], the family of 1D Fe(II) polymeric materials, with formula [Fe(4R-1,2,4-triazole$_3$)](anion)$_2$ showing thermal spin transition (ST) around the

✉ Yann Garcia
yann.garcia@uclouvain.be

1   Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain, Place L. Pasteur 1, 1348 Louvain-la-Neuve, Belgium

2   Department of Electrical Engineering and Computer Science & Research Center MANSiD, "Stefan cel Mare" University, University Street, No. 13, Suceava 720229, Romania
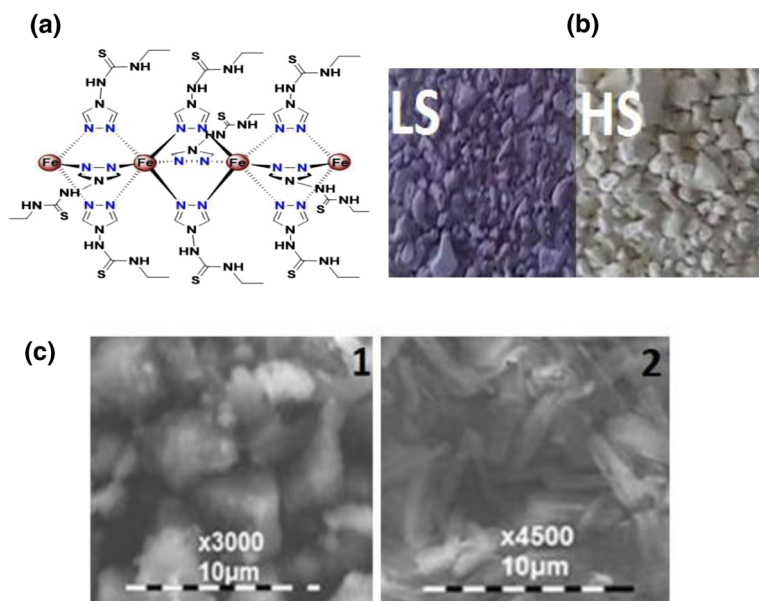
Fig. 1 **a** Schematic representation of the polymeric [Fe(4R-trz)$_3$]$_2^{2+}$ chains under study. **b** Reversible thermochromism from white (HS) to dark purple (LS) upon cooling to N$_{2(l)}$ temperature. **c** SEM images of microcrystalline particles of **1** and **2**

room temperature region, appears as potential targets for inclusion into electronic devices [2].We have prepared a new series of bridging 1,2,4-triazole ligands with a variable structural features that strongly coordinates iron(II) to form 1D chains. We chose in this work the ligand 1-ethyl-3-(4H-1,2,4-triazol-4-yl) thiourea (**Etutrz**) and present herein the synthesis and physical characterization by means of magnetic susceptibility measurements, Mössbauer spectroscopy, differential scanning calorimetry of two members of this new family of 1D spin crossover polymers with general formula [Fe(**Etutrz**)$_3$](Anion)$_2$·nSolvent.

2 Experimental

The **Etutrz** ligand was synthesized following a reported procedure [4]. Compounds **1** and **2** were synthesized by mixing **Etutrz** (200 mg, 1.16 mmol) dissolved in methanol (10 mL) and a methanolic solution (5 mL) of Fe(BF$_4$)$_2$·6H$_2$O (131 mg, 0.39 mmol) for **1**, or Fe(ClO$_4$)$_2$·6H$_2$O (100 mg, 0.39 mmol) for **2**, with a pinch of ascorbic acid in a vial. The mixture was stirred for 45 min to afford a white precipitate, which was filtered, washed with methanol and dried 24h with a dessicator. (**1**) IR: BF$_4^-$: 1087 cm^{-1}. Anal. Calc. for C$_{17}$H$_{35}$B$_2$F$_8$FeN$_{15}$O$_2$S$_3$ (807.2 g.mol^{-1}) C 25.30, H 4.37, N 26.02%. Found: C 25.14, H 2.69, N 26.12%. Yield: 65%. (**2**) IR: ClO$_4^-$: 1104 cm^{-1}. Anal. Calc. for C$_{15}$H$_{29}$Cl$_2$FeN$_{15}$O$_9$S$_3$ (786.42 g.mol^{-1}): C 22.40, H 3.88, N 26.12. Found: C 22.95, H 3.82, N 26.07%. Yield: 70%. Based on elemental and thermogravimetric analysis (only for **1**), the complexes were formulated as [Fe(Etutrz)$_3$](BF$_4$)$_2$·2MeOH (**1**) and [Fe(Etutrz)$_3$](ClO$_4$)$_2$·1.5H$_2$O (**2**). SEM image on bulk sample of **1** shows highly aggregated 1 μm diameter amorphous particles and needles for **2** (Fig. 1c). The crystallinity of **1** and **2** was confirmed by X-ray powder diffraction. Mössbauer spectra were recorded in
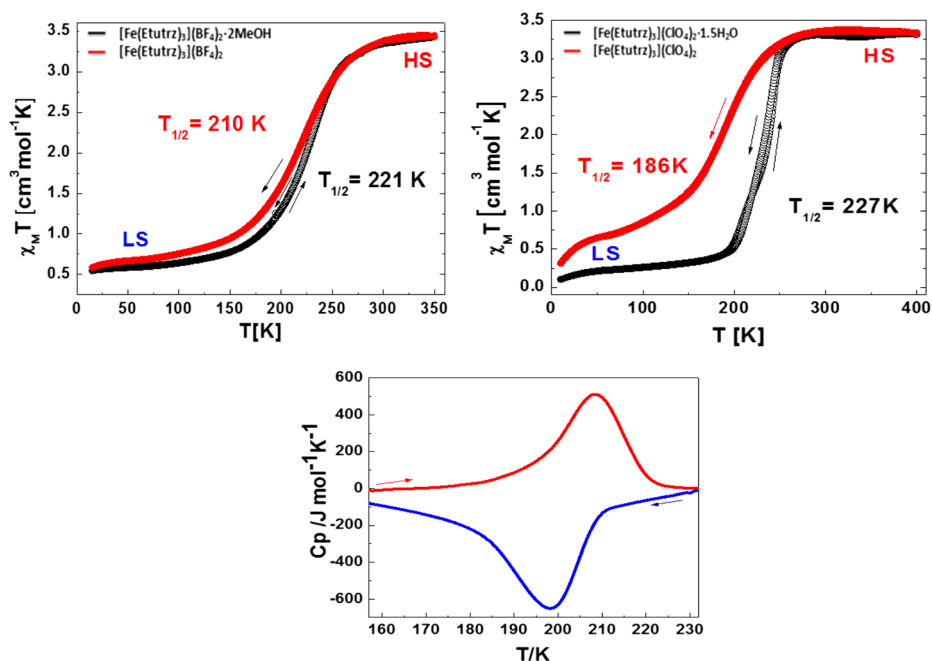
Fig. 2 (top) $\chi_M T$ vs. T of [Fe(Etutrz)$_3$](BF$_4$)$_2$·2MeOH (**1**) and [Fe(Etutrz)$_3$](ClO$_4$)$_2$·1.5H$_2$O (**2**). On cooling ($\leftarrow$) and warming ($\rightarrow$) modes (bottom) DSC curve of **2** on cooling ($\leftarrow$) and warming ($\rightarrow$) modes

transmission geometry using an Elssin spectrometer equipped with a Cyclotron Ltd ^{57}Co(Rh) source operating at room temperature, and fitted to an Oxford Instruments bath cryostat for low temperature measurements. Powdered samples were packed between pure aluminium foils and inserted onto the sample rod. Spectra were fitted to a sum of Lorentzians by least-squares refinement using Recoil 1.05 Mössbauer Analysis Software [5]. All isomer shits and quadrupole splittings are given with respect to α-iron calibration at room temperature. Magnetic susceptibilities were measured in the temperature range 4-300 K using a Magnetic Property Measurement System (MPMS®3) SQUID magnetometer operating at 1000 Oe. Data were corrected for magnetization of the sample holder and diamagnetic contributions, which were estimated from the Pascal constants. Differential scanning calorimetry measurements were carried out in a He$_{(g)}$ atmosphere using a Perkin-Elmer DSC Pyris instrument, operating at 10 °C/min, equipped with a liquid nitrogen cryostat operating down to 108 K and an integration module for specific heat determination [6]. Thermogravimetric analysis was performed in air over the range 25–400 °C at a scan rate of 10 °C/min.

3 Results and discussion

The magnetic properties of **1** and **2** were investigated using a SQUID following a thermal sequence to enable coverage of both solvated and desolvated samples: (i) cooling from room temperature to 4 K. (ii) warming up to 350 K (for **1**) or 400 K (for **2**) to ensure dehydration. (iii) cooling to 4 K. A gradual SCO profile is observed for **1** with $T_{1/2}$ = 221 K. No
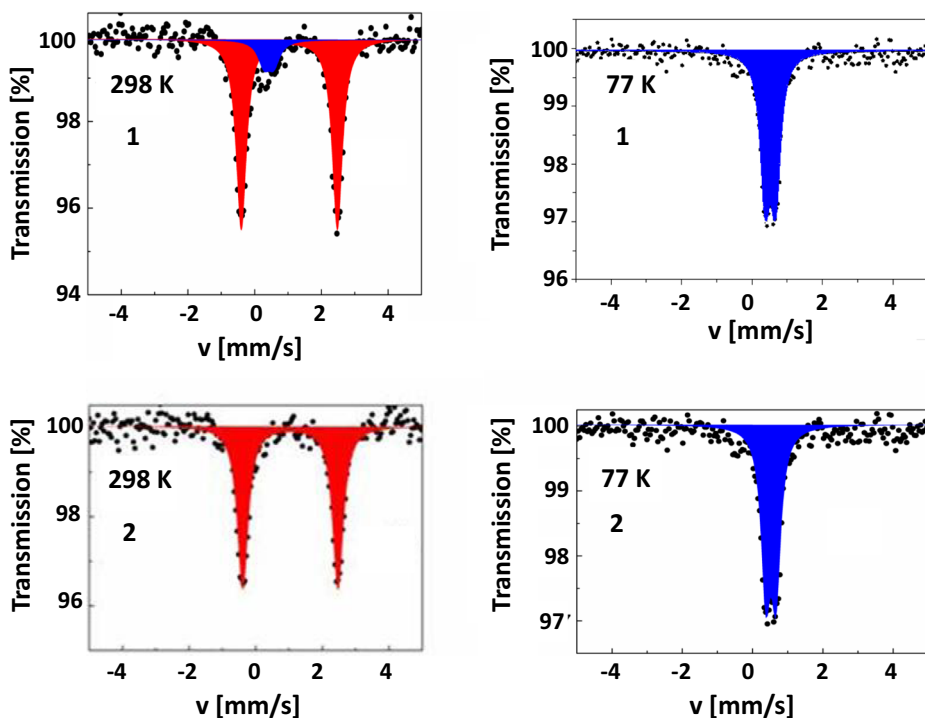
Fig. 3 Selected ^{57}Fe Mossbauer spectra for **1** and **2.** Blue and red signals stand for LS and HS doublets, respectively

hysteresis effect is observed. A similar gradual transition is also observed for the desolvated sample with $T_{1/2} = 210$ K. For **2**, a different situation is encountered since this material displays a more complete and sharper SCO behavior which is shifted upwards at $T_{1/2} = 227$ K. After dehydration, an incomplete and gradual transition is observed with $T_{1/2} = 186$ K, contrasting with the behavior of the hydrated compound. The comparison of this transition temperature with the one of the desolvated sample of **1**, is in agreement with the trend predicting a decrease of $T_{1/2}$ upon inclusion of a larger non coordinated anion in 1D chains (e.g. ClO_4^- by BF_4^-) [6]. Comparison with the $T_{1/2}$ of solvated complexes of **1** and **2** is not relevant due to the different solvation degree and nature, which are expected to set up different internal pressure in the crystal lattice.

Due to its sharp SCO behavior, **2** was selected for differential scanning calorimetric (DSC) measurements, which were performed over the temperature range 100–310 K. The molar heat capacities at constant pressure, C_p, show on warming an endothermic peak at $T^{\uparrow}_{max} = 208$ K, and on cooling an exothermic peak at $T^{\downarrow}_{max} = 198$ K, thus revealing a hysteresis loop of width 10 K (Fig. 2). This behavior is characteristic of a first-order phase transition and can be related to the SCO detected by magnetic measurements studies. The shift in temperature and the increase of hysteresis width for DSC compared to SQUID measurements can be assigned to the increase of scan rate. The enthalpy and entropy variation have been evaluated as $\Delta H = 12.4$ kJ mol^{-1} and $\Delta S = 61.3$ J mol^{-1} K^{-1}. The vibrational contribution to the entropy variation is evaluated as $\Delta S_{vib} = 47.97$ J K mol^{-1}. The origin of the highly cooperative spin transition observed in **2** can be assigned to the supramolecular

Table 1 Overview of selected ^{57}Fe Mössbauer parameters for **1** and **2**

T [K]	HS [mm/s]			LS [mm/s]			A_{HS}/A_{tot}
	δ	ΔE_Q	$\Gamma/2$	δ	ΔE_Q	$\Gamma/2$	
1 298(1)	1.04(8)	2.88(2)	0.18(1)	0.43(8)	0.30(4)	0.21(1)	88
1 78(1)	–	–	–	0.53(2)	0.3(4)	0.13(3)	0
2 298(1)	1.04(1)	2.86(2)	0.16(1)	–	–	–	100
2 78(1)	–	–	–	0.53(2)	0.29(2)	0.13(3)	0

δ: isomer shift (with respect to α-Fe at 298 K); ΔE_Q: quadrupole splitting; $\Gamma/2$: half width at half maximum

organization of non coordinated water molecules in the crystal lattice, that upon removal, leads to a disorganized structure, and therefore a gradual SCO behavior as observed on the desolvated sample (Fig. 2).

^{57}Fe Mössbauer spectra of **1** and **2** are shown in Fig. 3 and hyperfine parameters are summarized in Table 1. Spectra were studied both at room temperature and 77 K to track the spin state change of these materials. For **1**, a quadrupole doublet with isomer shift $\delta = 1.04(8)$ mm.s^{-1} and quadrupole splitting $\Delta E_Q = 2.88(2)$ mm.s^{-1} is observed at 298 K. Such hyperfine parameters with a large electric field gradient is characteristic of HS Fe(II) ions (Fig. 3). A similar δ is observed for **2**, indicating that the coordination sphere is not affected by the counter anion and solvent modification. The quadrupole splitting slightly decreases to $\Delta E_Q = 2.86(2)$ mm.s^{-1}. Another doublet is detected for **1** at 298 K with $\Delta E_Q = 0.30(4)$ mm.s^{-1}, which is characteristic of LS Fe(II) ions . No LS Fe(II) ions were found at 298 K for **2**. On cooling to 77 K, a single quadrupole doublet corresponding to LS Fe(II) ions is identified for **1** and **2** at $\delta = 0.53(2)$ mm.s^{-1}, indicating a complete spin transition. The low ΔE_Q of 0.3 mm.s^{-1} matches the one of distorted LS Fe(II) octahedral within 1D chains with 4-amino-1,2,4-triazole [6]. No Fe(III) species were detected confirming the success of the synthesis of these 1D materials.

4 Conclusion

We have presented the magnetic and calorimetric properties of two new 1D iron(II) coordination polymers featuring reversible spin crossover behavior on cooling These results are important for the establishment of a database of temperature sensors, e.g. for civil security applications [7]. Our laboratory is pursuing efforts in this direction.

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