Hyperfine Interact
DOI 10.1007/s10751-013-0909-3

Spin conversion detected by Mössbauer spectroscopy and μSR on a 1D Fe^{II} paramagnetic chain

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Abstract While magnetic properties of the 1D chain $[Fe(hyetrz)_3](4\text{-bromophenylsulfonate})_2$ investigated over the temperature range from 300 K to 2 K show paramagnetic behavior, detailed ^{57}Fe Mössbauer and muon spin relaxation measurements reveal an unexpected spin conversion. Approximately ∼14 % of the high-spin ions are found to convert to the low-spin state with a transition temperature $T_{1/2} \sim 120$ K.

Keywords ^{57}Fe Mossbauer spectroscopy · Muon spin relaxation · Coordination polymers · Spin crossover · 1,2,4-triazole

Proceedings of the 32nd International Conference on the Applications of the Mössbauer Effect (ICAME 2013) held in Opatija, Croatia, 1–6 September 2013.

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Published online: 13 November 2013

1 Introduction

Spin crossover (SCO) molecular switches are considered as potential components of memory devices, displays and sensors [1, 2]. Among SCO materials, one-dimensional Fe^{II} 1,2,4-triazole chain compounds continue to attract a great deal of attention due to their remarkable magnetic properties, sometimes observed around room temperature [3]. Owing to the spin multiplicity of Fe^{II} ions ($S = 2$) and the deviations from their isotropic environments, zero-field splitting (ZFS) may also be encountered at helium temperatures [4]. In the present work, we present a spin state tracking investigation of the coordination polymer, $[Fe(hyetrz)_3](4\text{-bromophenylsulfonate})_2$ (hyetrz = 4-2′-hydroxyethyl-1,2,4,-triazole). We have established that while this polymer reveals a high-spin (HS) behaviour over the temperature range from 300 K to 2 K from its magnetic measurements profile, the polymer shows clear spin conversion features from both ^{57}Fe Mössbauer and muon spin relaxation (μSR) spectroscopies.

2 Results

$[Fe(hyetrz)_3](4\text{-bromophenylsulfonate})_2$ was synthesized using a common procedure adapted from [5]. The variable temperature magnetic measurements were carried out on a Quantum Design MPMS2 SQUID susceptometer operating at 1 T. Experimental data were corrected for diamagnetism using Pascal's constants. For μSR measurements on the MUSR spectrometer at the ISIS facility, a powdered white sample was inserted into an aluminium mount and covered with a Mylar film window. The holder was masked from the muon beam by a silver plate. The μSR data were recorded in longitudinal geometry using a closed-cycle refrigerator, and analyzed using the WiMDA software [6], considering Lorentzian and Gaussian components for data fitting using the function $a(t) = a_F e^{-\lambda_F t} + a_s e^{-[(\sigma)_s t]^2} + a_{bg}$. Mössbauer spectra were recorded in transmission geometry using a spectrometer equipped with a ^{57}Co(Rh) source operating at room temperature, and fitted to an Oxford Instruments bath cryostat for variable temperature measurements. The spectra were fitted to a sum of Lorentzian lineshapes by least-squares refinement using Recoil 1.05 Mössbauer Analysis Software [7].

The material under investigation is made of a cationic coordination polymer and of aromatic counter-anions which stand in the space between chains (Fig. 1). The magnetic properties of $[Fe(hyetrz)_3](4\text{-bromophenylsulfonate})_2$ recorded over the temperature range 2–300 K reveal a very slight decrease of the $\chi_M T$ product on cooling down to 50 K, which is consistent with an $S = 2$ ground state. The decrease in $\chi_M T$ at lower temperature is in agreement with the presence of ZFS and a weak antiferromagnetic (AF) interaction between HS spins (Fig. 1). The temperature dependence of the initial asymmetry, a_o, derived from Zero-field (ZF) μSR data recorded over the temperature range (12–300 K) show a deviation from the magnetic measurement on cooling, which becomes more pronounced below ~75 K. This unusual behaviour – the deviation of a_o from the bulk magnetic behaviour – may indicate the presence of an unexpected spin conversion with an amount of switching spins which is below the detection limit of the bulk measurement technique but which could, none the less, be detected by ^{57}Fe Mössbauer spectroscopy.

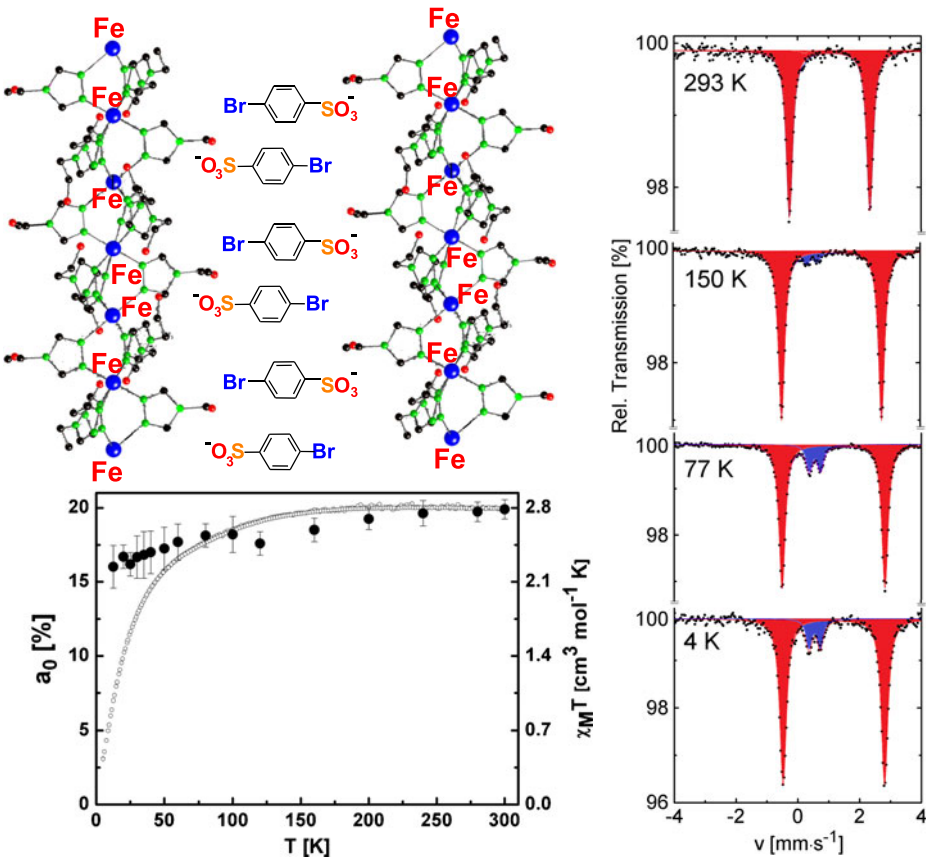

Fig. 1 (*Left; lower*) Comparison between the temperature dependence of $\chi_M T$ (1 T) and a_o (closed symbols with error bars; ZF measurements) derived from zero-field μSR spectroscopy over the temperature range 2–300 K. A schematic view of the structure of [Fe(hyetrz)$_3$](4-bromophenylsulfonate)$_2$ is also presented. (*Right*) Selected ^{57}Fe Mössbauer spectra of [Fe(hyetrz)$_3$](4-bromophenylsulfonate)$_2$ at the temperatures indicated identifying a spin state conversion from HS signal (in *red*) to LS signal (in *blue*)

Table 1 ^{57}Fe Mössbauer parameters for [Fe(hyetrz)$_3$](4-bromophenylsulfonate)$_2$

T [K]	A_{HS}/A_{tot} [%]	HS [mm/s]			LS [mm/s]		
		δ	ΔE_Q	$\Gamma/2$	δ	ΔE_Q	$\Gamma/2$
293(1)	100	1.04(1)	2.60(1)	0.12(1)	–	–	–
150(1)	95.6(1)	1.13(1)	3.23(1)	0.12(1)	0.50(3)	0.32(5)	0.10(4)
100(1)	89(1)	1.15(1)	3.31(2)	0.12(2)	0.56(1)	0.38(1)	0.12(1)
77(1)	86.1(1)	1.15(1)	3.32(1)	0.12(1)	0.55(1)	0.36(1)	0.12(1)
4(1)	87.6(2)	1.16(1)	3.29(1)	0.12(1)	0.54(2)	0.36(3)	0.10(2)

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

The Mössbauer spectrum recorded at room temperature confirms the paramagnetic nature of the material with a quadrupole doublet with parameters ($\delta = 1.04(1)$ mm.s^{-1} and $\Delta E_Q = 2.60(1)$ mm.s^{-1}) consistent with a HS Fe^{II} 1,2,4-triazole chain

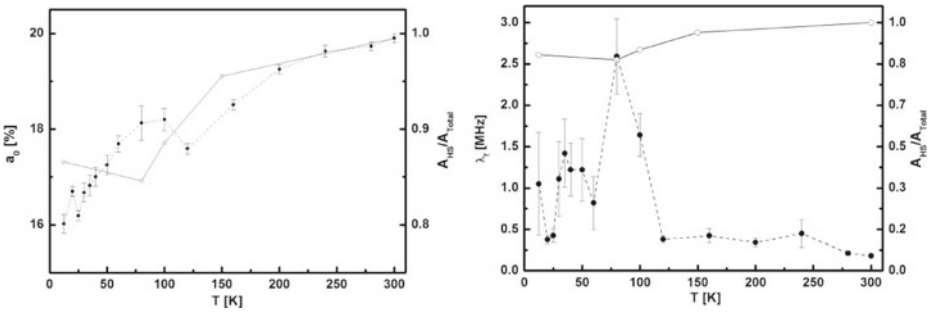

Fig. 2 (*Left*) Comparison between a_o (closed symbols; *left scale*) and A_{HS}/A_{tot} (*right scale*) as derived by μSR and Mössbauer spectroscopy respectively over the temperature range 12–300 K. (*Right*) Temperature dependence of the fast relaxation rate, λ_F, of the μSR signal (closed symbols; *left scale*). The evolution with temperature of A_{HS}/A_{tot} is shown again for convenience (*right scale*). The lines act as guides to the eyes

complex (Fig. 1). Most interestingly, on cooling to around 150 K a new signal appears with the following parameters ($\delta = 0.50(3)$ mm.s^{-1} and $\Delta E_Q = 0.32(5)$ mm.s^{-1}), values which are characteristic of distorted low-spin (LS) Fe^{II} ions, as expected for a constrained octahedron within a polymeric chain [8]. This signal grows in intensity with decreasing temperature, and reaches a sub-spectral fraction of ∼14 % at 4 K (assuming equal Debye Waller factors for all spin species; Table 1). This behaviour constitutes a clear indication of a HS ↔ LS conversion with a transition temperature $T_{1/2} \sim 120$ K. The evolution of the HS area, A_{HS}/A_{tot}, is in rather good agreement with the a_o values derived from analyses of the μSR signals (Fig. 2). Also significant is that an anomaly in the fast relaxation rate, λ_F, has been detected in the vicinity of the transition temperature (Fig. 2).

3 Conclusions

Wehave carried out a set of magnetic and Mössbauer spectroscopy experiments supported by μSR spectroscopy on the coordination polymer $[Fe(hyetrz)_3](4\text{-bromophenylsulfonate})_2$ (hyetrz = 4-2′-hydroxyethyl-1,2,4,-triazole). Comparisons of the outcomes from these techniques demonstrate the key role of Mössbauer spectroscopy, not only in detecting a HS ↔ LS conversion with transition temperature $T_{1/2} \sim 120$ K, but also in quantitative evaluation of the HS/LS population in iron complexes for which magnetic measurements indicate a paramagnetic state. These findings are supported by analyses of the μSR relaxation signals which reveal a deviation in the initial asymmetry parameter, a_o, and a pronounced anomaly in the fast relaxation rate, λ_F, around the transition temperature. Given this knowledge, we anticipate that literature reports of the behaviour of some HS iron complexes may warrant reassessment as a result of the insight provided by a combination of Mössbauer and μSR techniques [9].

Acknowledgements We acknowledge support from the European Union under Framework 5 for access to the MUSR instrument at the ISIS Facility, Rutherford Appleton Laboratory, U.K, and support from the Fonds National de la Recherche Scientifique-FNRS, the Romanian Academy and WBI-Roumanie. S.J.C. acknowledges support from the Access to the Major Research Facilities

Program, Australian Nuclear Science and Technology Organisation. His attendance at ICAME2013 is supported in part by the Australian Research Council (DP110102386). V.K. and P.G. are grateful for financial support from the German Science Foundation (Priority Program 1137). We also thank F. Varret for his help during Mössbauer data collection at 4 K. We thank the Fonds pour la Recherche dans l'Industrie et dans l'Agriculture for a doctoral scholarship allocated to Y. B. and the FNRS-F.R.S. for a chargé de recherche fellowship allocated to M. M. D.

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