Spin state tuning in Fe^{II} 1D coordination polymers made of 1,2,4-triazol-4-yl-propanoic and butanoic acids

Antoine P. Railliet · Anil D. Naik · Pedro Castanho-Vaz · Aurelian Rotaru · Marian Grigoras · Nicoleta Lupu · Jacqueline Marchand-Brynaert · Yann Garcia

Abstract A series of four Fe^{II} coordination polymers [Fe(patrz)$_3$]Cl$_2$•2H$_2$O, [Fe(patrz)$_3$]Cl$_2$, [Fe(batrz)$_3$]Cl$_2$•2H$_2$O and [Fe(batrz)$_3$]Cl$_2$ was prepared with slight variations in the ligand framework (1,2,4-triazol-4-yl-propanoic acid (patrz) or 1,2,4-triazol-4-yl-butanoic acid (batrz)) and solvation (2H$_2$O or dry). Dramatic influence of chain length and solvent has been evidenced on magnetic properties. Spin crossover properties were carefully studied by temperature dependent SQUID magnetometry and ^{57}Fe Mössbauer spectroscopy. Thermodynamic parameters for [Fe(batrz)$_3$]Cl$_2$•2H$_2$O were determined by differential scanning calorimetry (DSC) allowing a simulation of the spin crossover behaviour and the quantification of the cooperativity.

Keywords ^{57}Fe Mössbauer spectroscopy · Coordination polymers · Spin transition · 1,2,4-Triazole · Cooperativity · Differential scanning calorimetry

1 Introduction

1,2,4-triazoles are known to give an intermediate ligand field strength in Fe^{II} coordination polymers where spin crossover (SCO) can occur [1]. Light irradiation, temperature, and pressure are external triggers that will impact electrons distribution

---

A. P. Railliet · A. D. Naik · P. Castanho-Vaz · J. Marchand-Brynaert · Y. Garcia (✉)
Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain,
Place L. Pasteur 1, 1348 Louvain-la-Neuve, Belgium
e-mail: yann.garcia@uclouvain.be

A. Rotaru
Faculty of Electrical Engineering and Computer Science, Stefan cel Mare University,
13, Str. Universitatii, Suceava 720229, Romania

M. Grigoras · N. Lupu
National Institute of Research and Development for Technical Physics, 700050 Iasi, Romania

Ⓐ Springer

between t_{2g} and e_g levels. As a result, the spin state of these materials can be reversibly switched between high-spin (HS, S = 2) and low-spin states (LS, S = 0). Many parameters like temperature domain, abruptness, hysteresis, completeness, fatigue resistance and chemical stability allow describing the wide diversity of magnetic behaviours of these materials [2]. Depending on those characteristics many applications are possible, ranging from molecular based information storage devices, to highly accurate sensors, including cold channel tracking [2–4].

A series of iron(II) SCO materials was recently designed using amino acid esters to build 1,2,4-triazoles [5–8]. Using amino acid instead of esters, a series of metal-organic frameworks with porous properties [9, 10] and new zinc complexes [11, 12] were obtained. We have shown that SCO conditions can also be met using amino acids [13], despite their potential coordinating effect, thus opening exciting perspectives in this field. Herein the essential role of azole units' nature on the spin state is evidenced by a comparison of SCO coordination polymers made of two very similar functionalized amino acid derivatives.

2 Experimental

Ligands 3-(4H-1,2,4-triazol-4-yl)propanoic acid (**patrz**) and 4-(4H-1,2,4-triazol-4-yl)butanoic acid (**batrz**) are respectively derived from β-alanine and γ-aminobutyric acid according to the reported procedure [14]. These ligands which are reacted with $FeCl_2 \bullet 4H_2O$ in a methanolic solution and precipitated as powders, were filtered and dried in air at room temperature. Based on elemental analyses and thermogravimetric measurements, complexes were formulated as $[Fe(patrz)_3]Cl_2 \bullet 2H_2O$ (**1**$\bullet$2H$_2$O): Anal. for $FeC_{15}H_{25}N_9O_8Cl_2$: Found (calculated). C, 30.16 (30.74); H, 4.15 (4.30); N, 20.66 (21.51) and $[Fe(batrz)_3]Cl_2 \bullet 2H_2O$ (**2**$\bullet$2H$_2$O): Anal. for $FeC_{18}H_{31}N_9O_8Cl_2$: Found (calculated). C, 34.28 (34.41); H, 4.65 (4.97); N, 19.98 (20.07).

3 Results and discussion

Both patrz and batrz ligands show neat $\nu_{(C=O)}$ around 1730 cm^{-1} in IR spectra which are unaffected in **1**$\bullet$2H$_2$O and **2**$\bullet$2H$_2$O that confirms the neutral nature of the ligand and thus the non-involvement of carboxylic moiety in coordination. Coordination occurs exclusively from the bridging 1,2,4-triazole and affords 1D coordination polymers [1]. Those powders have amorphous textures as shown by Scanning Electron Microscopy (SEM) (Fig. 1) and confirmed by poor X-ray powder diffraction patterns.

Magnetic data of solvated complexes were first recorded over the temperature range 4–300 K. Influence of ligand structure on the spin state is clearly evidenced. While **1**$\bullet$2H$_2$O remains LS over the 4–300 K range [13], **2**$\bullet$2H$_2$O shows an abrupt and hysteretic spin transition (ST), with a square shaped hysteresis loop at $T_c^{\downarrow} = 248(1)$ K and $T_c^{\uparrow} = 256(1)$ K (Fig. 2, red curves).

In addition (knowing that hydration can have a crucial influence on the spin state [15]), the samples were warmed up to 400 K and maintained at this temperature for 10 min so as to remove non-coordinated solvent molecules and measurements were repeated (Fig. 2, green curves). After complete dehydration which was checked
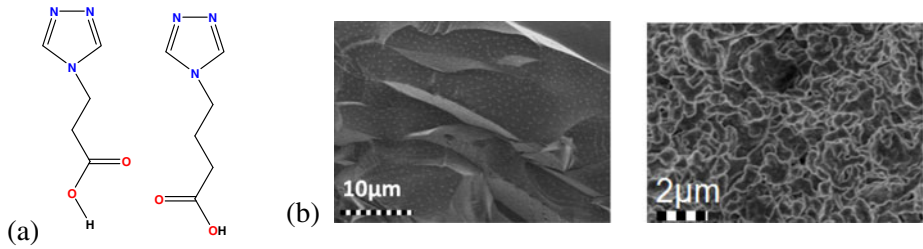
Fig. 1 **a** Molecular structures of **patrz** and **batrz**. **b** SEM images on **1**•2H$_2$O [6] and **2**•2H$_2$O
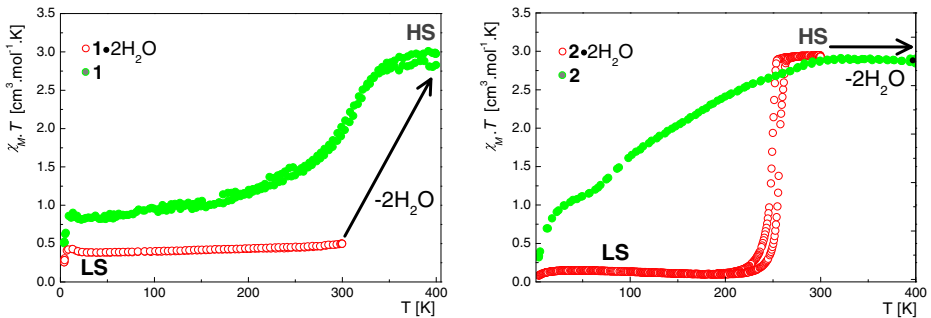
Fig. 2 $\chi_M.T$ *vs. T* plot for **1**•2H$_2$O and **1** (*left*) [13]; **2**•2H$_2$O and **2** (*right*)
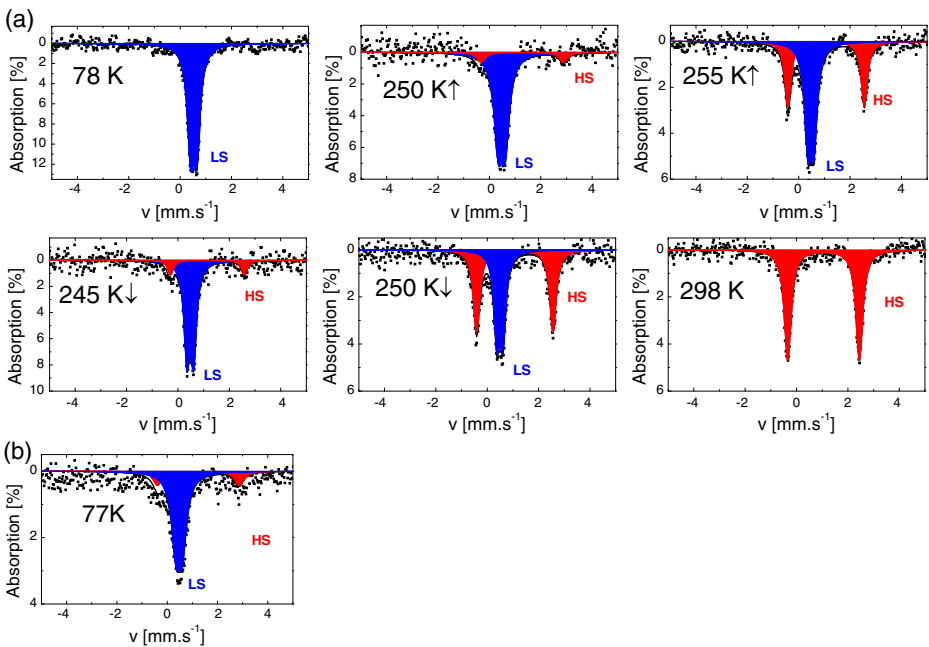
Fig. 3 ^{57}Fe Mössbauer spectra of **a** **2**•2H$_2$O showing the hysteretic behaviour of the ST, **b** **1**•2H$_2$O containing a little residual HS at 77 K

Table 1 ^{57}Fe Mössbauer parameters for **1**•2H$_2$O and **2**•2H$_2$O

	T [K]	A$_{HS}$/A$_{tot}$ [%]	HS [mm/s]			LS [mm/s]		
			δ	ΔE$_Q$	Γ/2	δ	ΔE$_Q$	Γ/2
1•2H$_2$O	77(1)	15(8)	1.15(9)	3.5(2)	0.2(1)	0.52(2)	0.24(3)	0.16(3)
2•2H$_2$O	78(1)	0	–	–	–	0.53(1)	0.24(1)	0.15(1)
	190(1)↑	0	–	–	–	0.50(2)	0.21(5)	0.22(4)
	240(1)↑	0	–	–	–	0.48(2)	0.24(4)	0.21(3)
	250(1)↑	16(13)	1.2(2)	3.1(5)	0.4(4)	0.48(2)	0.28(3)	0.19(3)
	255(1)↑	40(4)	1.07(1)	2.98(2)	0.15(2)	0.48(1)	0.24(2)	0.22(9)
	260(1)↑	83(4)	1.07(1)	2.93(1)	0.15(1)	0.45(4)	0.2(2)	0.2(1)
	270(1)↑	100	1.07(1)	2.90(2)	0.16(1)	–	–	–
	298(1)	100	1.05(1)	2.79(2)	0.16(1)	–	–	–
	260(1)↓	100	1.07(1)	2.93(2)	0.15(2)	–	–	–
	250(1)↓	53(4)	1.08(2)	2.97(3)	0.15(2)	0.49(2)	0.24(2)	0.14(2)
	245(1)↓	14(7)	1.15(6)	2.9(2)	0.14(9)	0.48(2)	0.26(2)	0.14(2)
	240(1)↓	0	–	–	–	0.49(1)	0.24(2)	0.15(2)

δ : isomer shift (with respect to α-Fe at 298 K); ΔE$_Q$: quadrupole splitting; Γ/2: half width at half maximum
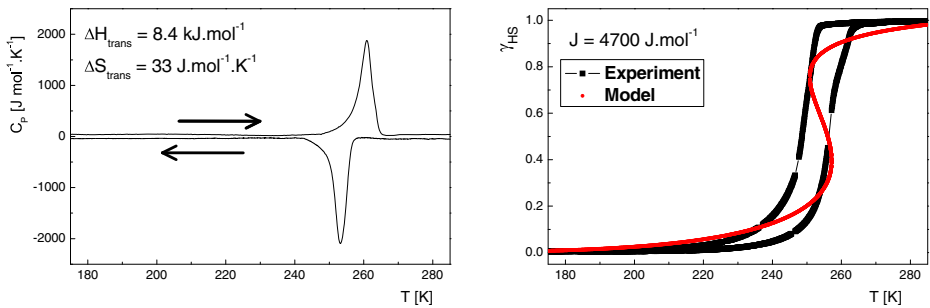
Fig. 4 (*Left*) DSC curve of **2**•2H$_2$O on cooling (←) and warming (→) modes. (*Right*) Fit between γ$_{HS}$, derived by SQUID measurements and by the Slichter and Drickamer model

by thermogravimetric measurements, it was found that both ligand field strength and cooperative effects are dramatically affected. Indeed, a gradual and incomplete magnetic profile was observed for both **1** and **2**. In particular, the 1D chain **2** reveals on cooling two anomalies around 260 K and 100 K, with a narrow plateau around 60 K, after which zero-field splitting is observed at lower temperature. These experiments demonstrate the crucial role played by non-coordinated water molecules on the spin state.

^{57}Fe Mossbauer spectra on **2**•2H$_2$O confirm the complete ST behaviour with a 100% HS population at 298 K ($\delta^{HS} = 1.05(1)$ mm/s; $\Delta E_Q^{HS} = 2.79(2)$ mm/s) converted to LS at 78 K ($\delta^{LS} = 0.53(1)$ mm/s; $\Delta E_Q^{LS} = 0.24(1)$ mm/s) (Fig. 2). A bistable character is clearly evidenced by comparing the significant difference between the spectra at 250 K on warming and cooling modes (Fig. 3, Table 1).

Differential Scanning Calorimetry (DSC) of **2**•2H$_2$O provides thermodynamic parameters associated to the spin transition. Scanning with 10 K.min^{-1}, enthalpy and entropy variations associated to the ST were respectively integrated as $\Delta H_{trans} = 8.4$ kJ.mol^{-1} and $\Delta S_{trans} = 33$ J.mol^{-1}.K^{-1} (Fig. 4).

Fitting of the HS molar fraction (γ_{HS}) derived from Fig. 2 with Slichter and Drickamer model [16] allowed quantifying the cooperativity associated to the spin transition, on a first approximation (Fig. 4). An intermolecular interaction factor J = 4.7 kJ.mol^{-1} > 2RT$_{trans}$ has been obtained, confirming tendencies on the cooperative behaviour observed from others 1,2,4-triazole based iron(II) SCO compounds [17].

4 Conclusion

This study carried out on the very same 1D system [Fe(Rtrz)$_3$]Cl$_2\bullet$nH$_2$O (n = 2, 0), show that upon increasing the chain length on the 4-R triazole substituent, the HS state is systematically stabilized. A similar observation was made when increasing the counter anion size in such systems [18]. Similarly, the interchain spacing could be modified. With a highly desired gradual spin crossover around room temperature [19], compound **1** is a nice example of room temperature sensor [13], operational after solvent release. Thanks to its abrupt and hysteretic spin transition, **2**$\bullet$2H$_2$O is thought to be proposed as a model spin crossover system within this substance class, e. g. for pressure studies.

References

1. Garcia, Y., Niel, V., Muñoz, M.C., Real, J.A.: Top. Curr. Chem. **233**, 229 (2004)
2. Linares, J., Codjovi, E., Garcia, Y.: Sensors **12**, 4479 (2012)
3. Garcia, Y., Ksenofontov, V., Gütlich, P.: Hyperfine Interact. **139/140**, 543 (2002)
4. Garcia, Y., Ksenofontov, V., Mentior, S., Dîrtu, M.M., Gieck, C., Bhatthacharjee, A., Gütlich, P.: Chem. Eur. J. **14**, 3745 (2008)
5. Dîrtu, M.M., Naik, A.D., Marchand-Brynaert, J., Garcia, Y.: J. Phys. Conf. Ser. **217**, 012085 (2010)
6. Dîrtu, M.M., Schmit, F., Naik, A.D., Rotaru, A., Marchand-Brynaert, J., Garcia, Y.: Int. J. Mol. Sci. **12**, 5339 (2011)
7. Naik, A.D., Dîrtu, M.M., Railliet, A.P., Marchand-Brynaert, J., Garcia, Y.: Polymers **3**, 1750 (2011)
8. Dîrtu, M.M., Schmit, F., Naik, A.D., Rotaru, A., Marchand-Brynaert, J., Garcia, Y.: Hyperfine Interact. **205**, 69 (2012)
9. Naik, A.D., Dîrtu, M.M., Léonard, A., Tinant, B., Marchand-Brynaert, J., Su, B.L., Garcia, Y.: Cryst. Growth Des. **10**, 1798 (2010)
10. Dîrtu, M.M., Neuhausen, C., Naik, A.D., Léonard, A., Robert, F., Marchand-Brynaert, J., Su, B.L., Garcia, Y.: Cryst. Growth Des. **11**, 1375 (2011)
11. Naik, A.D., Beck, J., Dîrtu, M.M., Bebrone, C., Tinant, B., Robeyns, K., Marchand-Brynaert, J., Garcia, Y.: Inorg. Chim. Acta **368**, 21 (2011)
12. Naik, A.D., Tinant, B., Léonard, A., Marchand-Brynaert, J., Su, B.L., Garcia, Y.: Cryst. Growth Des. **11**, 4034 (2011)
13. Railliet, A.P., Naik, A.D., Rotaru, A., Marchand-Brynaert, J., Garcia, Y.: Hyperfine Interact. **205**, 51 (2012)

14. Naik, A.D., Marchand-Brynaert, J., Garcia, Y.: Synthesis **1**, 149 (2008)
15. Garcia, Y., van Koningsbruggen, P.J., Lapouyade, R., Rabardel, L., Kahn, O., Wieczorek, M., Bronisz, R., Ciunik, Z., Rudolf, M.F.: C. R. Acad. Sci. Paris **IIc**, 523 (1998)
16. Slichter, C.P., Drickamer, H.G.: J. Chem. Phys. **56**, 2142 (1972)
17. Roubeau, O., Castro, M., Burriel, R., Haasnoot, J.G., Reedijk, J.: J. Phys. Chem. B **115**, 3003 (2011)
18. Dîrtu, M.M., Rotaru, A., Gillard, D., Linares, J., Codjovi, E., Tinant, B., Garcia, Y.: Inorg. Chem. **48**, 7838 (2009)
19. Šalitroš, I., Madhu, N.T., Boča, R., Pavlik, J., Ruben, M.: Monatsch. Chem. **140**, 695 (2009)