

1D iron(II) spin crossover complexes with 1,2,4-triazol-4-yl-propanoic acid

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Abstract A series of 1D coordination polymers $[\text{Fe}(\text{patrz})_3]\text{X}_2\cdot\text{solv}$, (*patrz* = 1,2,4-triazol-4-yl-propanoic acid; $\text{X} = \text{BF}_4^-, \text{ClO}_4^-, \text{Cl}^-, \text{NO}_3^-$ and *solv* = MeOH or H_2O) were precipitated from methanol. Their spin crossover properties were studied by temperature dependent SQUID magnetometry and ^{57}Fe Mössbauer spectroscopy, both for solvated and desolvated complexes. Compounds show gradual incomplete spin crossover with distinct thermochromism, in particular $[\text{Fe}(\text{patrz})_3](\text{BF}_4)_2\cdot\text{MeOH}$, for which only 27% of Fe^{II} ions are switched to the low-spin state at 77 K, as determined by a detailed ^{57}Fe Mössbauer study. Other prominent features of this work are the interesting self assembly of 1D chain with exclusively triazole coordination from *patrz* ligand despite its ditopic nature and a hysteretic room temperature spin crossover in $[\text{Fe}(\text{patrz})_3]\text{Cl}_2$.

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

1 Introduction

Iron(II) spin crossover (SCO) materials exhibit the remarkable property of molecular bistability with rapid optical and magnetic feedback to external perturbations that could offer an attractive prospect for future molecular based information storage

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devices [1, 2]. Among several factors that influence SCO, ligand design plays a crucial role. In this context, 1,2,4-triazole derivatives represent privileged candidates to prepare well-organized coordination polymers [3] which should lead to abrupt SCO with hysteresis loops ranging over a wide temperature domain. Recently β -amino acid derivatives have been successfully introduced as suitable precursors to build 1D coordination polymers exhibiting abrupt, hysteretic SCO around room temperature [4, 5]. This prompted us to employ a new analogous ligand derived from β -amino acid series. We report herein on the spin state properties of a series of 1D iron(II) complexes of formula $[\text{Fe}(\text{patrz})_3](\text{anion})_2 \cdot \text{solv}$, with $\text{patrz} = 1,2,4\text{-triazol-4-yl-propanoic acid}$.

2 Experimental

The patrz molecule was obtained following the reported procedure [6]. Iron complexes were prepared by mixing 1 eq. of iron salts with 3 eq. of patrz in methanolic solutions affording white or pink/purple powders that were isolated at room temperature and dried in air. Based on elemental analysis and thermogravimetric analyses, complexes were formulated as $[\text{Fe}(\text{patrz})_3](\text{BF}_4)_2 \cdot \text{MeOH}$ (**1**-MeOH, white solid), $[\text{Fe}(\text{patrz})_3](\text{ClO}_4)_2 \cdot \text{MeOH}$ (**2**-MeOH, white solid), $[\text{Fe}(\text{patrz})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (**3**-2H₂O, purple solid) and $[\text{Fe}(\text{patrz})_3](\text{NO}_3)_2 \cdot \text{MeOH}$ (**4**-MeOH, pink solid).

3 Results and discussion

Infrared spectral analysis of complexes shows prominent bands around 1060 cm^{-1} (**1**-MeOH), 1090 cm^{-1} (**2**-MeOH), 1385 cm^{-1} (**4**-MeOH), which confirms the presence of non-coordinated anions BF_4^- , ClO_4^- and NO_3^- , respectively. The neat $\nu_{(\text{C}=\text{O})}$ observed at 1730 cm^{-1} in patrz is seen around the same value for all complexes. Both observations prove the non-involvement of carboxylic moiety suggesting the neutral nature of the ligand. Thus the coordination is assumed to occur exclusively from the bridging 1,2,4-triazole. Bulk samples were all analyzed by Scanning Electron Microscopy (SEM) revealing diversity in texture (Fig. 1), as well as an amorphous nature, the latter was also confirmed by poor X-ray powder diffraction patterns.

Magnetic data of all solvated complexes were recorded over the temperature range 4–300 K. In addition, the samples were warmed up to 400 K (except for **2**-MeOH due to risk of explosion from perchlorate anion) and maintained at this temperature for 10 min so as to remove non-coordinated solvent molecules and measurements were repeated (Fig. 2a, b). A gradual decrease of the $\chi_M T$ product of $3.47\text{ cm}^3\text{ K mol}^{-1}$ is observed on cooling from room temperature for **1**-MeOH with $T_{1/2} = 128\text{ K}$ (Fig. 2a). The profile is slightly altered for **1**, with $T_{1/2} = 112\text{ K}$ after solvent removal (Fig. 2a). This magnetic behavior corresponds to a gradual incomplete spin conversion. Profile is similar in **2**-MeOH with $T_{1/2} = 138\text{ K}$. The drop below 50 K is presumably due to the zero-field splitting for remaining high-spin (HS) Fe^{II} ions (Fig. 2a) [7]. Magnetic properties, recorded over the temperature range 4–300 K, for **3**-2H₂O and **4**-MeOH are typical for low-spin (LS) complexes. A few iron ions remain however in the HS state, with a slightly higher proportion in **4**-MeOH

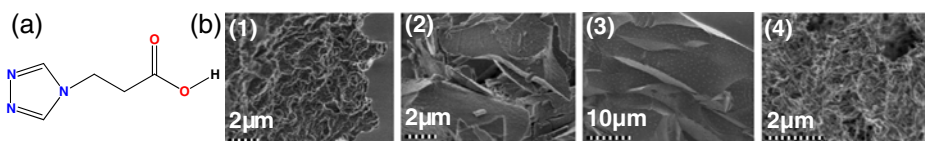


Fig. 1 **a** Molecular structure of patrz. **b** SEM images on **1–4**: highly aggregated particle of ~ 200 nm (**1**:MeOH), amorphous solids (**2**:MeOH and **3**: $2\text{H}_2\text{O}$) and needles of ~ 100 nm length (**4**:MeOH)

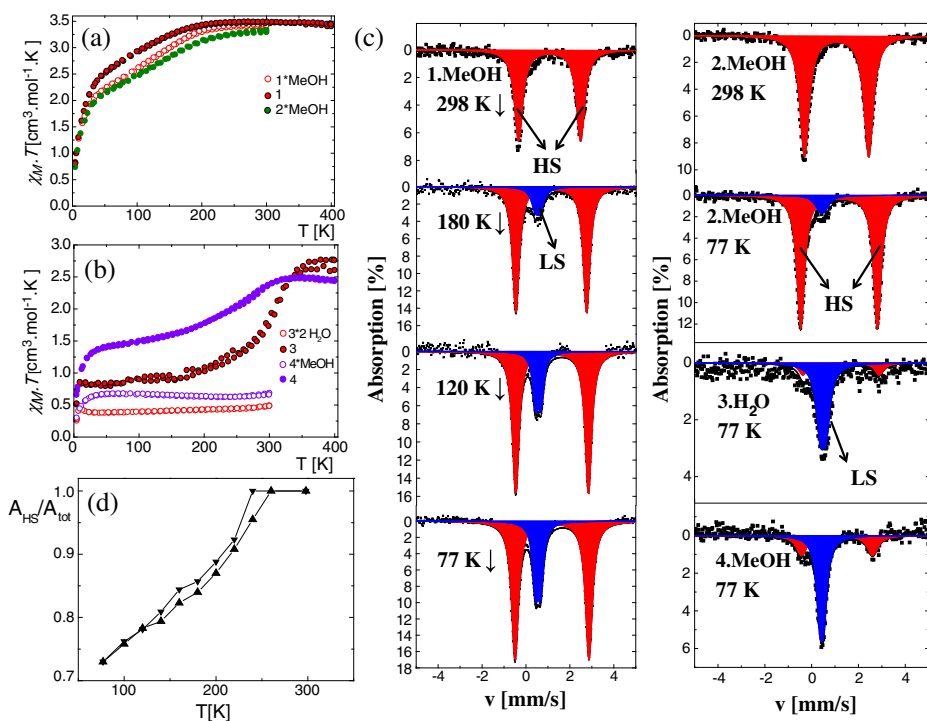


Fig. 2 $\chi_M T$ vs. T plot for the $[\text{Fe}(\text{patrz})_3](\text{anion})_2$ solvated (**a**) and desolvated series (**b**). (**c**) ^{57}Fe Mössbauer spectra for $[\text{Fe}(\text{patrz})_3](\text{anion})_2$ -solv complexes at selected temperatures. (**d**) $A_{\text{HS}}/A_{\text{tot}}$ vs. T for **1**:MeOH

(Fig. 2b). After solvent removal, there is a dramatic change in the magnetic behavior with significant increase of $\chi_M T$ ($2.77 \text{ cm}^3 \text{ K mol}^{-1}$ for **3** and $2.5 \text{ cm}^3 \text{ K mol}^{-1}$ for **4**) at 300 K. These desolvated complexes display on cooling a clear SCO to the LS state with $T_{1/2} = 294 \text{ K}$ for **3** and a gradual SCO behavior with $T_{1/2} = 233 \text{ K}$ for **4** (Fig. 2b). Remarkably the spin conversion curve is centered at room temperature for **3**, which has been rarely encountered [8], and is not complete in both HS and LS states. Such a room temperature SCO is highly sought for potential applications in molecular display and data storage devices [1, 2]. Indeed, insertion of more voluminous anions such as BF_4^- or ClO_4^- leads to the occurrence of SCO behavior at lower temperature (112–138 K) whereas smallest anions such as Cl^- or planar NO_3^- tends to stabilize the LS state and shifts the SCO behavior upwards (233–294 K) [9, 10].

Table 1 ^{57}Fe Mössbauer parameters for $[\text{Fe}(\text{patrz})_3](\text{anion})_2\text{-solv}$ complexes

	T [K]	$A_{\text{HS}}/A_{\text{tot}}$ [%]	HS [mm/s]			LS [mm/s]		
			δ	ΔE_Q	$\Gamma/2$	δ	ΔE_Q	$\Gamma/2$
1-MeOH	77	73(1)	1.18(1)	3.36(1)	0.19(1)	0.55(1)	0.24(1)	0.16(1)
	120 \uparrow	78(1)	1.17(1)	3.34(1)	0.19(1)	0.54(1)	0.24(1)	0.15(1)
	140 \uparrow	79(2)	1.16(1)	3.31(1)	0.19(1)	0.54(1)	0.24(2)	0.15(2)
	160 \uparrow	82(2)	1.15(1)	3.27(1)	0.19(1)	0.53(1)	0.22(3)	0.16(2)
	180 \uparrow	84(2)	1.14(1)	3.24(1)	0.19(1)	0.51(2)	0.20(4)	0.16(3)
	200 \uparrow	87(2)	1.13(1)	3.19(1)	0.19(1)	0.50(2)	0.24(4)	0.15(3)
	220 \uparrow	91(2)	1.11(1)	3.12(1)	0.19(1)	0.46(3)	0.2(1)	0.18(8)
	240 \uparrow	95(3)	1.10(1)	3.06(1)	0.21(1)	0.5(1)	0.2(4)	0.2(3)
	260 \uparrow	100	1.10(1)	2.99(1)	0.23(1)	–	–	–
	298	100	1.07(1)	2.83(1)	0.23(1)	–	–	–
	240 \downarrow	100	1.11(1)	3.05(1)	0.20(1)	–	–	–
	220 \downarrow	92(2)	1.11(1)	3.11(1)	0.19(1)	0.47(4)	0.23(8)	0.16(7)
	200 \downarrow	89(2)	1.13(1)	3.17(1)	0.19(1)	0.48(3)	0.20(9)	0.18(7)
	180 \downarrow	86(2)	1.14(1)	3.22(1)	0.19(1)	0.52(3)	0.23(9)	0.21(6)
	160 \downarrow	84(2)	1.15(1)	3.25(1)	0.18(1)	0.53(1)	0.23(3)	0.15(2)
	140 \downarrow	81(2)	1.16(1)	3.28(1)	0.19(1)	0.54(1)	0.25(2)	0.15(2)
	120 \downarrow	78(2)	1.17(1)	3.31(1)	0.19(1)	0.54(1)	0.25(2)	0.16(2)
100 \downarrow	76(2)	1.17(1)	3.33(1)	0.19(1)	0.56(1)	0.25(1)	0.14(1)	
2-MeOH	77(1)	91(2)	1.18(1)	3.28(1)	0.20(1)	0.45(4)	0.2(2)	0.2(1)
	298	100	1.07(1)	2.74(1)	0.24(1)	–	–	–
3-2H ₂ O	77(1)	15(8)	1.15(9)	3.5(2)	0.2(1)	0.52(2)	0.24(3)	0.16(3)
4-MeOH	77(1)	30(3)	1.17(2)	3.44(3)	0.20(3)	0.50(1)	0.21(2)	0.17(1)

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

^{57}Fe Mössbauer spectra were recorded between 77 and 300 K for all solvated complexes. Selected spectra, shown in Fig. 2c, are consistent with the magnetic properties described above. At 298 K, the spectra of **1**.MeOH ($\delta^{\text{HS}} = 1.07(1)$ mm/s and $\Delta E_Q^{\text{HS}} = 2.83$ mm/s) and **2**.MeOH ($\delta^{\text{HS}} = 1.07(1)$ mm/s and $\Delta E_Q^{\text{HS}} = 2.74(1)$ mm/s) are similar. On cooling to 77 K, a spin state conversion is confirmed with the growing of a LS doublet (in blue) with $\delta^{\text{LS}} = 0.55(4)$ mm/s and $0.45(4)$ mm/s for **1**.MeOH and **2**.MeOH, respectively. The HS doublet at 77 K (in red) indicates that a major fraction of Fe^{II} ions are not switched to the LS state. An incomplete spin conversion (only 27%) is thus detected as confirmed by the temperature dependence of $A_{\text{HS}}/A_{\text{tot}}$ shown in Fig. 2c for **1**.MeOH. This curve also confirms the gradual nature of the spin conversion that was suggested by SQUID measurements and which could be related to steric constraints in this system. This unusual situation prevents to undergo any reliable determination of Debye temperatures in both spin states [11].

The diamagnetic character of **3**-2H₂O and **4**-MeOH is confirmed by a major LS doublet (in blue), a few HS Fe^{II} ions (in red) being also detected by Mössbauer spectroscopy (Fig. 2c). These hyperfine parameters are consistent with HS and LS Fe^{II} complexes with a distorted pseudo-octahedral coordination geometry, and fall in the range of parameters described for analogous 1D chain complexes [4, 5, 10, 11]. These Mössbauer parameters are also in a good agreement with computed values derived from similar family of materials [12] (Table 1).

A novel series of 1D Fe^{II} complexes has been prepared using a ditopic 1,2,4-triazole ligand and their magnetic properties studied by SQUID magnetometry and

^{57}Fe Mössbauer spectroscopy. $[\text{Fe}(\text{patrz})_3]\text{Cl}_2$ display an hysteretic room temperature spin conversion whereas $[\text{Fe}(\text{patrz})_3](\text{BF}_4)_2 \cdot \text{MeOH}$ show a gradual and incomplete spin conversion on cooling. Nanostructuration of these functional materials towards their future implementation in next generation devices are continuing.

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