

Coordination preference and magnetic properties of Fe^{II} assemblies with a bis-azole bearing 1,2,4-triazole and tetrazole

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Abstract With a new bis-azole molecular fragment (**Htt**) bearing 1,2,4-triazole and tetrazole, a mononuclear complex [Fe(tt)₂(H₂O)₄]·2H₂O (**1**), a trinuclear complex [Fe₃(tt)₆(H₂O)₆]·2H₂O (**2**) and a 1D coordination polymer [Fe(tt)(Htt)₂]BF₄·2CH₃OH (**3**) were obtained by varying reaction conditions. **Htt** acts either as an anionic or neutral ligand depending upon the reaction medium and pH. Thermal variation of spin states of **1–3** were investigated in the range 77–300 K by ⁵⁷Fe Mössbauer spectroscopy. **1** totally remains in high-spin state over the entire temperature range whereas no spin crossover was evidenced in **2**. Nearly 1:1 high-spin and low-spin population ratio is found in **3**, which remains constant over the entire temperature range investigated.

Keywords ⁵⁷Fe Mössbauer spectroscopy · Coordination polymers · Spin-transition, 1,2,4-triazole

1 Introduction

Spin crossover (SCO) area continues to proliferate with the advent of new SCO materials, associated theories, and prospective applications [1–5]. In Fe^{II} SCO materials synthesized with suitably designed ligand system, the spin state of iron can be switched between high-spin (HS) and low-spin (LS) with the aid of external addressing parameters like temperature, pressure and light irradiation with an elegant read-out signal [1–5]. The phenomenal properties associated with such transition have high technological relevance that is proposed for the memory and display devices and as temperature/optical alerts in molecular sensors [1, 2]. The very basic requirement to fabricate SCO materials is the design of suitable ligand with appropriate ligand

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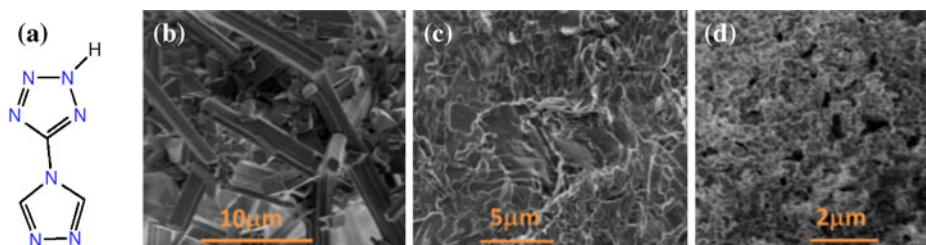


Fig. 1 **a** Molecular structure of **Htt**. **b–d** SEM images depicting morphologies on bulk samples of **1**, **2**, and **3**, respectively

field strength. An ideal ligand should also enhance the cooperativity among iron centers through its rigid framework and further through lattice by supramolecular interactions [4, 6]. In this context, we introduced a new nitrogen donor rich molecular fragment bearing two flagged motifs of 1,2,4-triazole and tetrazole (**Htt**) attached on a common platform. Both these precursors are independently very well recognized as excellent precursors in SCO area by demonstrating a wide range of coordinating capabilities, diverse topologies ranging from mononuclear complexes to high dimensional networks and exceptional SCO properties [1, 4, 6]. In the present work three new Fe^{II} assemblies with structural diversities are reported together with their magnetic properties investigated by ⁵⁷Fe Mössbauer spectroscopy.

2 Experimental

Synthesis of ligand (**Htt**) and complexes **1–3** (Fig. 1a) was carried out according to the reported procedure [7]. Reaction of **Htt** (100 mg) with [Fe(H₂O)₆](BF₄)₂ (82 mg) in water (30 mL, pH = 1) yielded colorless micro-crystals (**1**) within a week. Under similar experimental condition but with a minimum quantity of water (15 mL) a pink solid (**2**) was isolated within a day. If the same reaction is carried out in MeOH (pH = 3), immediately a pale pink solid is obtained (**3**).

3 Results and discussion

Elemental analysis, thermogravimetric (TGA) analysis, FT-IR supported the following compositions: a mononuclear complex [Fe(tt)₂(H₂O)₄].2H₂O (**1**), a trinuclear complex [Fe₃(tt)₆(H₂O)₆].2H₂O (**2**), and a 1D coordination polymer (CP) [Fe(tt)(Htt)₂]BF₄·2MeOH (**3**). The lability of proton attached to the tetrazole part in **Htt** is found to be sensitive to the reaction medium and significantly affects the structure and magnetic properties in **1–3**. Presence of coordinated and non-coordinated solvent molecules in **1–3** was deduced and quantified from TGA. In **1** and **2** coordinated water molecules are lost around 100°C and 120°C, respectively, whereas in **3**, non-coordinated methanol molecules are lost between 40–70°C. FT-IR spectra of **1** and **2** indicate absence of characteristic BF₄⁻ anion thus confirming that ligand acts as mono-anionic whereas **3** shows strong overlapped bands around 1080 cm⁻¹ which proves the presence of BF₄⁻ anion. SEM images on bulk samples

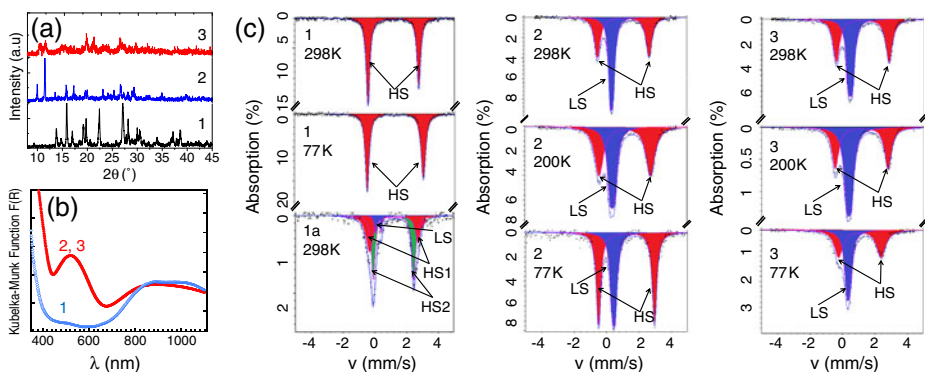


Fig. 2 a XRPD pattern for **1–3**. b DRS for **1** and **2**. c Mössbauer spectra of **1–3** at selected temperatures

shows $10 \times 1 \mu\text{m}$ rods (Fig. 1b) for **1**, randomly oriented blocks for **2** (Fig. 1c) and 100–150 nm diameter granules (Fig. 1d) for **3**. Signals in X-ray powder diffraction (XRPD) (Fig. 2a) are quite strong for **1** whereas it is weak but distinct in **2**. The poor diffractogram of **3** confirms amorphous nature found from SEM (Fig. 1d).

3.1 Spectroscopic studies

Diffuse reflectance spectrum (DRS) (Fig. 2b) of **1**, shows a broad band around 900 nm which corresponds to ${}^5T_{2g} \rightarrow {}^5E_g$ transition of HS Fe^{II} species. In addition, an additional band is found around 520 nm in **2** and **3** that correspond to ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition of LS Fe^{II} species thus proving the co-existence of both HS and LS species [2]. Colorless crystals of **1** and pink solid of **3** does not show thermochromism when quenched in N₂(l). The pink color of **2** turns to off-white when warmed to around 423 K, most presumably as a consequence of water release and stabilization of the HS state. CP **3** is highly sensitive and decomposes to brown solid upon warming. ⁵⁷Fe Mössbauer spectral study was undertaken over the temperature range 77–300 K to deduce the electronic and structural aspects of **1–3**. Selected spectra are displayed in Fig. 2 and parameters are grouped in Table 1.

At 298 K, the spectrum of **1** consists of a quadrupole split doublet with $\delta = 1.17(2)$ mm/s and $\Delta E_Q = 3.18(3)$ mm/s corresponding to HS state of Fe^{II}. Situation is similar at 77 K thus confirming absence of any spin state crossover. The asymmetry of the lines observed in the HS state is attributed to a texture effect. As expected, with water as weak coordinating ligand the situation is not favorable for a spin state switching. In air or under vacuum, **1** loses non-coordinated water molecules to give [Fe(tt)₂(H₂O)₄], **1a**. The appearance of a new HS signal along with a few LS species in Mössbauer spectrum (Fig. 2c) of desolvated complex (**1a**) suggests disruption of supramolecular network that leads to non-equivalent HS iron sites. Trinuclear complex **2** appears pink at 298 K but Mössbauer and DRS spectra at 298 K shows existence of both HS and LS species. In fact, **Htt** acts as an anionic ligand by deprotonation from its tetrazole part and bridges iron centers by its triazole counterpart. Thus, two types of iron centers are created, one with a central FeN₆ octahedron and two terminal FeN₃O₃ coordination spheres which are supported by

Table 1 ^{57}Fe Mössbauer parameters for **1–3**

Compound	T (K)	δ (mm/s)	ΔE_Q (mm/s)	$\Gamma/2$ (mm/s)	Species, %
1	298	1.17(2)	3.18(3)	0.18(2)	HS, 100
	77	1.25(2)	3.35(2)	0.19(2)	HS, 100
1a	298	1.18(3)	2.5(3)	0.17(2)	HS1, 50(2)
		1.21(3)	3.0(3)	0.18(2)	HS2, 42(2)
		0.23(3)	0.33(3)	0.19(2)	LS ^a , 8(3)
2	298	0.40(3)	0.15(4)	0.2(6)	LS, 55(4)
		1.14(5)	3.13(2)	0.22(2)	HS, 45(3)
	200	0.39(3)	0.26(2)	0.21(2)	LS, 43(4)
		1.16(4)	3.16(3)	0.25(2)	HS, 57(4)
	77	0.45(4)	0.19(2)	0.16(2)	LS, 36(3)
3	298	1.24(5)	3.44(2)	0.17(2)	HS, 64(4)
		0.35(2)	0.18(2)	0.19(2)	LS, 48(2)
	200	1.07(2)	2.62(2)	0.22(2)	HS, 52(4)
		0.37(3)	0.26(2)	0.25(3)	LS, 52(3)
		1.17(2)	3.28(2)	0.25(3)	HS, 48(2)
77	0.43(4)	0.23(3)	0.17(3)	LS, 48(4)	
		1.19(3)	3.23(2)	0.24(3)	HS, 52(4)

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

coordinated water molecules [6, 8]. At 77 K the major quadrupole doublet with $\delta = 0.45(4)$ mm/s and $\Delta E_Q = 0.19(2)$ mm/s corresponds to the LS state of central Fe^{II} ions and $\delta = 1.24(5)$ mm/s and $\Delta E_Q = 3.44(2)$ mm/s that corresponds to the HS state of terminal Fe^{II} ions are found with a relative intensity of 1:2. The presence of a small quadrupole splitting in the LS signal stems from a lattice contribution to the electric field gradient and therefore reveals a distorted character for the central LS octahedron. Subsequent warming at an interval of 50 K shows only slight changes in Mössbauer parameters. On warming to 298 K, the spectrum remains essentially the same, with the difference observed in the intensities of lines which can be attributed to the known difference in the Debye-Waller factors for the LS and HS states due to which the area fraction of both spin states do not reflect the actual concentration of the two species [6]. Spectrum above room temperature was not recorded due to risk of explosion from energetic tetrazole moiety. The spectrum of **3**, at 77 K corresponds to co-existence of HS and LS species roughly in 1:1 ratio and essentially remains constant upon warming to 298 K. The observed decrease in δ (Table 1) on warming from 77 K is due to relativistic second order Doppler shift [8].

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