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Cooperative 1D Triazole-Based Spin Crossover Fe^{II} Material With Exceptional Mechanical Resilience

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ABSTRACT: We report here the single crystal investigations, in both high spin (*HS*) and low spin (*LS*) states, correlated to magnetic and heat capacity measurements, of a new cooperative and robust spin crossover triazole-based Fe^{II} 1D coordination polymer $[Fe(bntrz)_3][Pt(CN)_4].H_2O$ (**1**) (bntrz = 4-(benzyl)-1,2,4-triazole). The compound exhibits a sharp transition at 240 K, accompanied with an anisotropic deformation of the unit cell and a significant gliding of the chains from each other. These two features are identified as the key parameters of the non-conventional mechanical resilience of this system.

The magnetic spin change associated to the spin crossover (*SCO*) phenomenon represents a paradigm of bistability at the molecular level which is of current interest because of potential applications in the development of new generations of electronic devices such as non-volatil memory, molecular sensing and displays.[1-5] The *SCO* phenomenon is especially observed in Fe^{II} complexes in which the paramagnetic high spin state (*HS*, $S = 2$) can be switched reversibly to the low spin state (*LS*, $S = 0$) by several external stimuli such as temperature, pressure or light irradiation.[6] A huge effort has been devoted to the understanding of the transition mechanisms using inter alia crystallographic tools.[7-8] The minimum requirements for the latter involve the determination of the crystal structures in both *LS* and *HS* states to comprehend the structural parameters at the molecular and inter-molecular scales. While some systems were deeply investigated due to their remarkable switching properties, the absence of any detailed and punctilious structural informations has precluded the definite understanding of these exciting properties. This is particularly the case of the so-called “triazole family”, more specifically coordination polymer chains of general formula $[Fe(Rtrz)_2(trz)](X)$, where Rtrz is a functionalised 1,2,4-triazole ligand and X a counter-anion, which typically display bistability with wide hysteresis loops around or above room temperature.[9-11] Although known for few decades, the major lack of high quality single crystals with complete structural data for those materials prevent any deep magneto-structural correlations which are of paramount importance for (i) the understanding of the origin of the thermal hysteresis loop, and (ii) the control of the transition temperature. Indeed, a deep knowledge of the structural data is required to evaluate notably the effects of the rigid triple $\mu_{1,2}$-trz bridges and/or the characteristics of the intramolecular contacts on the propagation of the elastic interactions. Owing to the great and intensifying attention given to these materials, scarce crystallographic investigations have been recently attempted. Among them, the structural characterizations of the *HS* and *LS* states of the $[Fe(Htrz)_2(trz)](BF_4)$ derivative, using distinctively high-resolution synchrotron X-ray powder diffraction combined with Raman spectroscopy[12] or X-ray diffraction data from high-quality crystalline powder,[13] have been reported. While the 1D chain structure was proven for both *HS* and *LS* states, the rather limited quality of the diffraction patterns could not provide highly precise structural data suitable for deep magneto-structural correlations. In the same time, a single crystal of the parent Cu^{II} compound $[Cu(NH_2trz)_3](NO_3)_2.3H_2O$ has been finely investigated by Garcia et al. to parallel with the crystal structure of the $[Fe(NH_2trz)_3](NO_3)_2$ for which only nano-sized thin crystallite needles (120-330 nm) could be prepared. However, the powder diffraction pattern of the latter did not fully fit to the diffraction pattern observed for the single crystals of the Cu^{II} compound.[10] Besides, the lone single crystal structural study proving the presumably 1D character of $[Fe(NH_2trz)_3](NO_3)_2.2H_2O$ was only reported in 2011 by Guionneau et al..[14] However, as clearly claimed by the authors, the very low diffraction pattern induced essentially by the sub-micrometric size (> 20x1x1 μm^3) of the crystals and the damages due to the X-ray beam during the data collection led to a rather low quality of the structural data which did not allow an accurate detailed discussion of the polymeric chain structure. In addition, the study, performed at 120 K, concerned only the *LS* state of the sample since the damages caused on the crystals when warming over room temperature have hindered data collection for the *HS* state. Ultimately, those recent examples clearly expose the challenge to access refined structural data in both spin states in order to fully apprehend and rationalize the conspicuous *SCO* properties in the Fe^{II}/trz systems.

In the last few years, some Fe^{II} systems based on functionalized triazole ligands (Rtrz) and different counter-anions have been reported.[11] However, the majority of the involved counter-ions are rather standard monoanions, while the functional groups (R) of the triazole molecules are essentially narrowed to linear or branched alkyl or alkoxylated chains.[11] Recently, we have extended this synthetic approach to combinations of triazole ligands and anions which were not used so far within the "triazole family"; among those combinations, triazole ligands involving rigid aryl groups with an alkyl spacer assuring the electronic integrity of the triazole motif, coupled with more sophisticated anions such as polycyanometallates or organic cyanocarbanions which display very diverse sizes, geometries and charges, have been initially considered.[15-16] In this ongoing work, we have realized at an early stage that this chemical approach involving these unusual building blocks tends to improve unprecedentedly the size, the quality and the robustness of the single crystals of the resulting original Fe^{II}/R-trz systems. Ultimately, this synthetic strategy should allow the access to single crystals of novel *SCO* cooperative materials, which is essential to understand the origin of the unparalleled cooperativity observed in those 1D coordination polymers. Thus, the present work reports the synthesis, the structural and magnetic characterizations, as well as the first accurate single crystal investigations of both *HS* and *LS* states of a new triazole-based *SCO* Fe^{II} 1-D polymer $[Fe(bntrz)_3][Pt(CN)_4].H_2O$ (**1**).

The bntrz ligand was prepared in two steps by reaction of triethyl orthoformate with formylhydrazine and benzylamine under nitrogen atmosphere (SI). Single crystals of $[Fe(bntrz)_3][Pt(CN)_4].H_2O$ (**1**) have been synthesized *via* diffusion technique in a fine glass tube (3.0 mm diameter) by layering an ethanolic solution of the bntrz ligand onto an aqueous solution containing both $K_2[Pt(CN)_4)].xH_2O$ and $Fe(BF_4)_2.6H_2O$ salts (SI). The magnetic susceptibility (χ_m) of **1** was measured over the 2-300 K temperature (T) range on a set of single crystals. The χ_mT versus T plot is displayed in Figure 1. In the high-temperature region, the χ_mT value (3.45 $cm^3.K.mol^{-1}$) is consistent with a *HS* (S = 2) configuration of the hexacoordinated Fe^{II} ions. Upon cooling, the χ_mT remains constant down to 240 K, then sharply decreases to *ca.* 0.0 $cm^3.K.mol^{-1}$, indicating the presence of a complete sharp *HS* to *LS* first-order spin transition ($T_{1/2}$ = 242 K). However, no significant thermal hysteresis effects were detected after the warming mode, at the value of the temperature scan rate of 0.4 $K.mn^{-1}$. The DSC measurements for **1**, performed in the temperature range 200-260 K with a temperature scan rate of 2 $K.mn^{-1}$, reveal exo- and endo-thermic transitions with maxima at 241.1 K and 243.5 K, respectively (Inset Figure 1). Furthermore, the phase transition has been found to occur with an enthalpy and entropy changes of ΔH = 16.87 $kJ.mol^{-1}$ and ΔS = 69.61 $J.K^{-1}.mol^{-1}$, respectively. These values are in the range of those reported in the literature for similar *SCO* compounds.[17] The presence of a weak hysteresis in the calorimetry data while it was absent in magnetic measurements can be reasonably attributed to the difference of temperature scan rates.

Based on the magnetic and calorimetric measurements, the crystal structure of **1**, defined in the triclinic space group, has been determined at 296 K (*HS* state, colourless crystal), and at 120 K (*LS* state, purple crystal) (Table S1). An in-depth examination of the unit cell parameters, at these two temperatures, indicates the absence of any symmetry breaking structural transition within the studied temperature range. The structure of **1** is built from two crystallographically independent Fe^{II} sites, Fe1 and Fe2, and two $[Pt(CN)_4]^{2-}$ anions located on inversion centers, and three bntrz ligands and one solvent water molecule located on general positions.

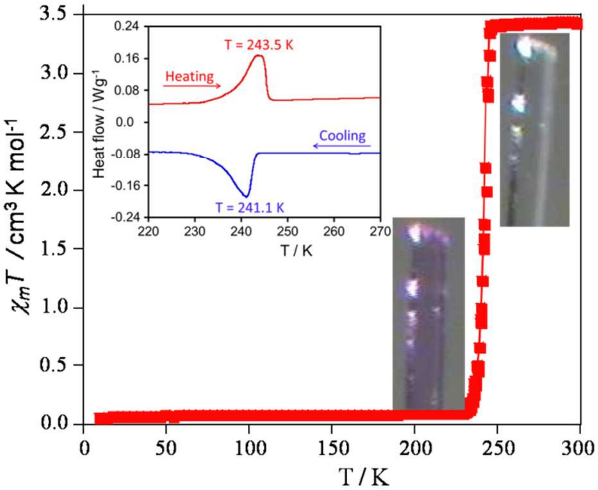

Figure 1. Thermal dependence of the χ_mT product recorded at 0.4 $K.mn^{-1}$ in a settle mode, DSC study recorded at 2 $K.mn^{-1}$ (inset), and crystal images in the *LS* and *HS* states showing the clear thermochromism from purple to colourless, respectively.

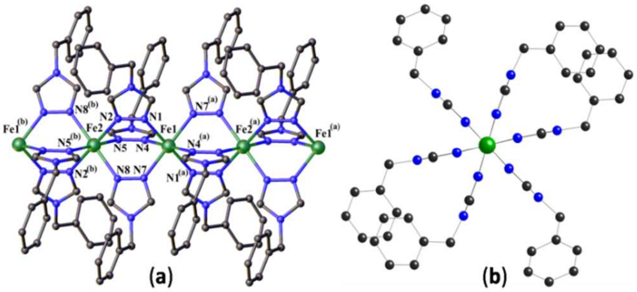

Figure 2. Views of the cationic chain in **1**: (a) linear chain running along the *a* axis; (b) projection of the chain along the [100] direction. (a) 1-x, -y, 1-z; (b) = -x, -y, 1-z.

The three bntrz ligands act as μ_2-bridging mode ($\mu_{1,2}$-bntrz bridges) leading to a regular chain structure running along the [100] direction (Figure 2). The average Fe-N distances and distortion parameters for both spin states are listed in Table 1. The selected Fe-N bond lengths and N-Fe-N bond angles, at 296 K and 120 K, are gathered in Table S2. The two crystallographically distinct Fe^{II} ions (Fe1 and Fe2) adopt similar and very regular FeN_6 octahedral geometries, as demonstrated by the unusually low values of Σ and Θ parameters (Table 1).[18] Thus, it is worth noting that the distortion of the octahedrons is higher in the *LS* state than in the *HS* state, conversely to what is generally observed. While more pronounced for Fe1 compared to Fe2, this unusual effect confirms that 1D triazole systems tend to adopt rigid and regular coordination spheres,[13] but also indicates that the Fe^{II} environment is more constrained in the *LS* state. The average values of the Fe-N distances, at 296 K (2.190(3), 2.189(3) Å) and 120 K (1.991(4), 1.998(4) Å), are in agreement with the presence of *HS* and *LS* states, respectively. The latter observation is consistent with the presence of a complete *HS/LS SCO* transition, as revealed by the magnetic data.

Table 1. Average Fe-N distances and distortion parameters in **1**.

T (K)	296		120	
Fe^{II}	Fe1	Fe2	Fe1	Fe2
$\langle d_{Fe-N}\rangle$ / Å	2.190(3)	2.189(3)	1.991(4)	1.998(4)
Σ / Θ / °	10/23	10/26	16/40	13/33
Spin state	*HS*	*HS*	*LS*	*LS*

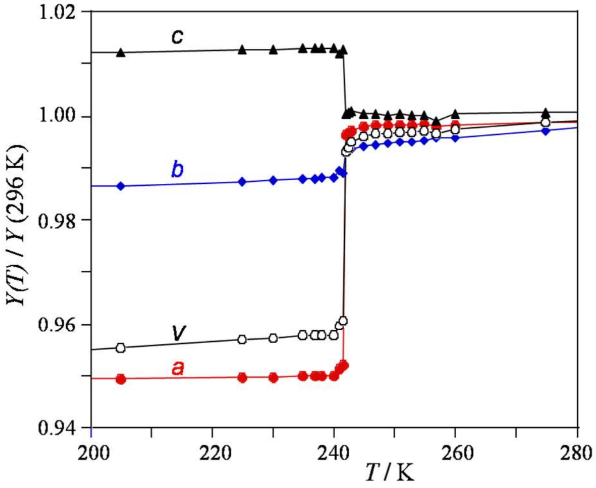

Figure 3. Thermal evolution of the lattice parameters for **1** showing the anisotropic changes upon *SCO* transition.

In order to understand how the crystal structure is affected by the *SCO* transition, the temperature dependence of the lattice parameters of a single crystal of **1** was measured in the range 200-280 K. As clearly depicted in Figure 3, the evolution of the unit cell parameters (*a, b, c)* reveals significant anisotropic changes at the transition temperature (*ca.* 242 K), more precisely a contraction upon heating for the *c* parameter paralleled with positive expansions occurring simultaneously in the *ab* plane. The amplitude of the anisotropic expansion is much more pronounced along the *a* axis, proving that the major structural change accompanying the *SCO* transition in the overall structure arises along the 1D chain. In comparison with the parent 1D compound [Fe(Htrz)$_2$(trz)](BF$_4$),[13] the careful examination of the shortest interchain contacts in **1** reveals the absence of direct H-bonding interchain interactions while strong direct H-bonding interchain interactions through the N-H group of the triazole have been identified in [Fe(Htrz)$_2$(trz)](BF$_4$) (Figures S1-S2). However, the presence of significant indirect H-bonding, occurring *via* the [Pt(CN)$_4$]$^{2-}$ anions, links the chains in the *b* and *c* directions, leading to an overall 3D packing (Figures 4 and S3). These interactions in **1** are more pronounced in the *LS* state than in the *HS* state; this observation may explain the more constrained iron geometry along the chain in the *LS* state. The intra-chain Fe···Fe distances in **1** are almost similar to the values than in [Fe(Htrz)$_2$(trz)](BF$_4$), in both spin states, while the inter-chain Fe···Fe ones are significantly longer than those observed in other parent 1D triazole-based derivatives that have been structurally characterized (see Table S3). Moreover, the Fe···Fe intra-chain distances in **1** appear also longer in both *HS* and *LS* states than the corresponding distances observed in discrete trinuclear complexes based on triazole ligands,[19-22] although this latter observation refers only to the few compounds that display 'full' *HS* or *LS* states i.e. involving all the iron centers. Due to the triclinic symmetry of the crystal lattice, the inter-chain distances do not exactly match the Fe···Fe intermolecular distances, but are shorter because the chains are slightly shifted from each other in the *a* direction (Figure S4). It follows that the inter-chain distances are different along the *b* and *c* directions. Thus, in the *LS* state, they are shorter in the *b* direction (14.2708(4) Å) compared to the *c* direction (14.5072(4) Å), while in the *HS* state, we observe the opposite tendency since the inter-chain distances along the *b* direction (14.4975(4) Å) are longer than those along the *c* axis (14.2832(4) Å), leading finally to very similar distances in the *LS* and *HS* states, but inverted with respect to *b* and *c* parameters (Figures S5-S6). These observations indicate a significant motion of the chains with respect to each other in the *bc* plane that co-occurs with a slight gliding along the *a* direction as the chains displacements increase during the *LS* to *HS* transition (*c.a.* 0.35 Å). Additionally, the *LS* to *HS* transition is accompanied by a rearrangement of the side chain of the triazole ligand, leading to a much better accommodation of the modification of the iron coordination sphere volume in **1** than in the parent compound [Fe(Htrz)$_2$(trz)](BF$_4$).[13] Indeed, while the octahedron volume (Vp) increases in similar proportion for both compounds (Vp increase of 32 % for **1** and 36 % for [Fe(Htrz)$_2$(trz)](BF$_4$)), the molecular volume remains almost the same for **1** (+0.8 %) but increases appreciably for [Fe(Htrz)$_2$(trz)](BF$_4$) (+4.7 %, Table S3). This structural rearrangement of the chains and the related accommodation of the molecular volume to the transition might be responsible for the smaller unit cell volume change at the transition when compared to the parent compound [Fe(Htrz)$_2$(trz)](BF$_4$) (4.5 % vs 11.5 %).[13] Such capability of structural breathing was not observed in [Fe(Htrz)$_2$(trz)](BF$_4$) and may explain the (i) unusual crystal quality of compound **1** and its (ii) exceptional reliability and mechanical resilience to repeated *LS* to *HS* transition. The latter has been clearly evidenced by crystal mosaïcity studies and optical microscopy investigations performed over 20 *SCO* cycles. Thus, (i) the crystal mosaïcity was found to be nearly constant around 0.49(2) between the *LS* and *HS* states (Figure S7), and (ii) no damage or alteration at the resolution of the optical microscopy (~0.3 micron) was detected within the single crystal (Figure S8). In addition, an elongation of 5.3 % of the crystal upon *LS* to *HS* transition was observed in optical microscopy studies. This value is in excellent agreement with X-rays data which indicates an elongation of 5.32 % of the *a* parameter during the *LS/HS* thermal transition.

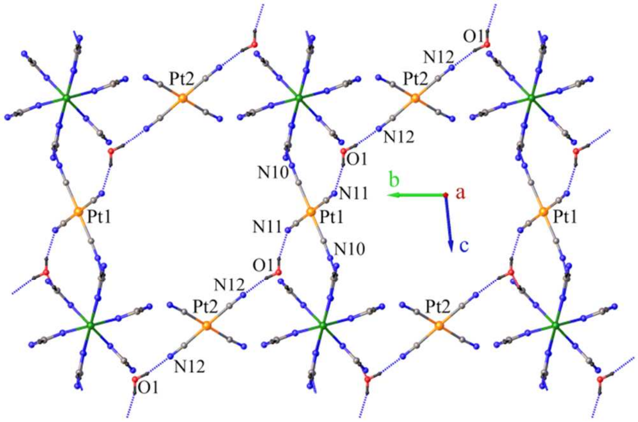

Figure 4. Intermolecular hydrogen bonding contacts in **1** (**a**) along the *a* direction. Shortest contacts (Å): N11…O1 = 2.944, O1…N12 = 2.995 at 296 K; N11…O1 = 2.888, O1…N12 = 2.883 at 120 K.

In conclusion, we have prepared and characterized a new triazole-based [Fe(bntrz)$_3$][Pt(CN)$_4$].H$_2$O (**1**) salt exhibiting an abrupt spin transition with a transition temperature of *ca.* 242 K. The cationic [Fe(bntrz)$_3$]$^{2+}$ complex displays a polymeric chain, similar to that reported for the Fe^{II} triazole-based systems exhibiting magnetic bistability around or above room temperature.[11-14] The present study clearly evidences the starring roles of the ligand substitution and counterion changes to prevail over the implicit crystallogenesis issue in the Fe^{II}/trz systems, with the association of bntrz ligand and $[Pt(CN)_4)]^{2-}$ anion leading for the first time to robust single crystals of high quality and relatively considerable size (up to 0.45 × 0.04 × 0.04 mm^3) that withstand the *LS/HS* first-order spin transition upon repeated *SCO* cycles. Distinctively from other 1D Fe^{II}/trz systems for which the origin of the strong cooperativity remains strictly indefinite because of the lack of structural information, the characteristics of complex **1** led us to single crystal X-ray data collections of high-quality, allowing highly refined structural characterizations of both high and low spin states, and the thermal evolution of the lattice parameters. The polymeric chain structure of **1**, crystallographically determined at 296 K and 120 K, is built from two different Fe^{II} centers for which the average values of the Fe-N distances are in agreement with the complete *HS/LS* spin transition revealed by the magnetic data. The crystal structures of the *LS* and *HS* states definitely confirm the perfect linearity of the chains of such polymeric triazole based *SCO* compounds, even in the *HS* state conversely to what was suggested from the first investigations based on EXAFS and WAXS studies.[23,24] The thermal variation of the lattice parameters shows anisotropic changes at the transition temperature, and proves that the most pronounced structural changes occur along the 1D covalent chain. The intermolecular inter-chain contacts occur through hydrogen bonding *via* the $[Pt(CN)_4]^{2-}$ anions leading to an overall 3D arrangement. Although displaying cooperativity, the absence of a wide hysteresis loop in the *SCO* of **1** reveals that the strong short-range ″Fe^{II}-$(Rtrz)_3$-Fe^{II}″ interactions along the chain are not sufficient to drive the existence of long lifetime metastable states at the origin of thermal hysteresis; it also confirms that the overall long-range interactions, with an emphasis on the direct contacts between the chains, should play a crucial role to promote significant elastic strains which stabilizes the spin state changes. The exceptional resilience of the present crystals upon repeated switching cycles is most likely due to the accommodation of the molecular volume and the anisotropic expansion/contraction of the unit cell upon *SCO* transition, which allows the existence of a mismatch free *HS/LS* interface resulting from the capability of the “Fe^{II}-(Rtrz)” chains to glide from each other and accommodate the structural modifications despite the sharp transition. This observation is similar to that of the spin-crossover single crystals $[\{Fe(NCSe)(py)_2\}_2(m\text{-}bpypz)]$ (with py = pyridine and bpypz = 3,5-bis(2-pyri-dyl)pyrazolate) recently reported by K. Boukhedadden et al..[25] In this context, we are currently investigating by optical microscopy the response of a single crystal of **1** upon thermal *SCO* transition in order to visualize the nucleation, the growth, and the propagation of *HS* and *LS* domains accompanying the first-order transition.[26] The observation of the orientation and the dynamics of the *HS/LS* interface should allow for a better understanding of the role of the anisotropic changes of the lattice parameters on the exceptional resilience of this material. On the other hand, we are also currently exploring other systems exhibiting similar chain, but with different crystal packing to enhance/control the interchain interactions and produce hysteretic features. *In fine*, the aim is to establish thorough and systematic magneto-structural correlations which are essential to understand the physicochemical origin of the strong cooperativity in such striking materials, but also to rationalize the tuning of the *SCO* properties.

ASSOCIATED CONTENT

Experimental details, syntheses of the ligands, the complex **1** and characterizations, X-ray crystallographic data in CIF format (CCDC 1492971 and 1492972), and additional structural data (Tables S1-S3, Figures S1-S8). This material is available free of charge *via* the Internet at http://pubs.acs.org.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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