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# The 1-D polymeric structure of the $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ (with $n = 2$ ) spin crossover compound proven by single crystal investigations†

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**The first single crystal-based description of a spin transition compound from the patented  $[\text{Fe}(\text{Rtrz})_3]\text{X}_2 \cdot n\text{H}_2\text{O}$  family is reported, properly the compound with  $\text{Rtrz} = 4\text{-amino-1,2,4-triazole}$ ,  $\text{X} = \text{NO}_3$  and  $n = 2$ . This study definitively proves the 1-D polymeric nature of the crystal structure and allows a description of the  $[\text{Fe}(\text{Rtrz})_3]$  chains, as well as of the anions and water implementation within the crystal lattice opening the possibility of subsequent investigations of the structure-property correlation within this peculiar family of spin transition compounds.**

Among the widely studied Spin Crossover (SC) solids within biology,<sup>1</sup> geology<sup>2</sup> or material science fields,<sup>3</sup> very few undergo a spin transition under daily thermodynamic conditions, *i.e.* the so-called room temperature and ambient pressure. This is nevertheless the case for the  $[\text{Fe}(\text{Rtrz})_3](\text{anion})_2 \cdot n\text{H}_2\text{O}$  spin crossover Fe(II) compounds family, known for about four decades to present spin transition with hysteresis centred around room temperature at ambient pressure<sup>4–7</sup> ( $\text{R} = \text{NH}_2$  or  $\text{H}$ ;  $\text{trz} = 1,2,4\text{-triazole}$ ). This family of spin transition compounds are the focus of patents<sup>6</sup> based on their X-chromism in such external conditions and have been the topic of numerous publications<sup>4–8</sup> around their physical and chemical properties, including the effect of particle size reduction.<sup>7</sup> Despite the paramount interest of this family, no absolute experimental proof of their crystal structure yet exists. The main reason is that single crystals have never been obtained, even though relatively well crystallized powders are now obtainable.<sup>7d</sup> Structural investigations with various strategies have nevertheless been attempted. Among these, the first study has been done by X-ray absorption techniques that allowed formulation of the hypothesis of a Fe atom alignment within the material, providing a possible model based on an unusual 1-D polymeric structure.<sup>8</sup> In parallel, researchers attempted to reach the crystal structure of the Fe(II) compounds by crystallizing  $[\text{M}(\text{Rtrz})_3]\text{X}_2 \cdot n\text{H}_2\text{O}$  compounds, where M is another metal,

such as copper. A very recent result shows, for example, an accurate structure of the  $[\text{Cu}(\text{NH}_2\text{trz})_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  compound, which indeed crystallizes as infinite  $\text{Cu}(\text{NH}_2\text{trz})_3$  chains, but in the meantime the powder diffraction pattern of the Fe and Cu analogues appear to be completely different.<sup>9</sup> Another very recent publication reports the first crystal structure deduced from powder X-ray diffraction for this  $[\text{Fe}(\text{Rtrz})_3]\text{X}_2 \cdot n\text{H}_2\text{O}$  family, more precisely for  $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$  ( $\text{Htrz} = 1,2,4\text{-}H\text{-triazole}$  and  $\text{trz} = 1,2,4\text{-triazolate}$ ).<sup>10</sup> However, the poor diffraction pattern quality, mainly due to the nano-sized crystallites, did not allow an accurate description of the structure, even the space group being questionable, for example. Note that the crystal structure of a chain SC compound has already been determined, but in such a case the ligand used, (tetrazole-1-yl)propane, was very different in nature and much more rigid than Rtrz, leading to a very gradual spin conversion.<sup>11</sup> All of the above studies have brought the assumption that the peculiar behaviour of the  $[\text{Fe}(\text{Rtrz})_3](\text{anion})_2 \cdot n\text{H}_2\text{O}$  spin crossover family notably originates in a crystal structure based on infinite  $[\text{Fe}(\text{Rtrz})_3]$  rigid chains. But, so far, no definitive proof had been obtained. We present in this paper the first crystal structure of a spin crossover compound of the  $[\text{Fe}(\text{NH}_2\text{trz})_3]\text{X}_2 \cdot n\text{H}_2\text{O}$  family based on a single crystal X-ray diffraction investigation, allowing not only a description of the chains, but also the first description of the interchain interactions. The  $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$  compound is already known to exhibit a thermal spin transition above room temperature with a large hysteresis.<sup>4</sup>

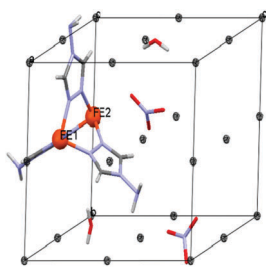
Single crystals were obtained by the slow diffusion method. A solution of  $\text{Fe}(\text{NO}_3)_2$  at  $0.67 \text{ mol L}^{-1}$  was initially put into a small diameter tube and immediately covered with a small volume of water, used to separate it from a solution of  $\text{NH}_2\text{trz}$  at  $2 \text{ mol L}^{-1}$ . Within a few days in ambient conditions, sub-micrometric needle-shaped transparent violet crystals grew in urchin-like clusters. One needle with a length of  $20 \mu\text{m}$  and others of dimensions inferior to  $1 \mu\text{m}$  were isolated and mounted on a Bruker X8 proteum rotating anode at the Cu-K $\alpha$  wavelength and cooled to 120 K. The system features the Microstar micro-focus X-ray source with the PLATINUM135 CCD detector combined with the 4-circle KAPPA goniometer and the Helios multilayer graded optics. This combination probably provides one of the most intense existing laboratory X-ray sources, which was necessary due to the weak diffraction pattern displayed by the samples. The downside, however, is that

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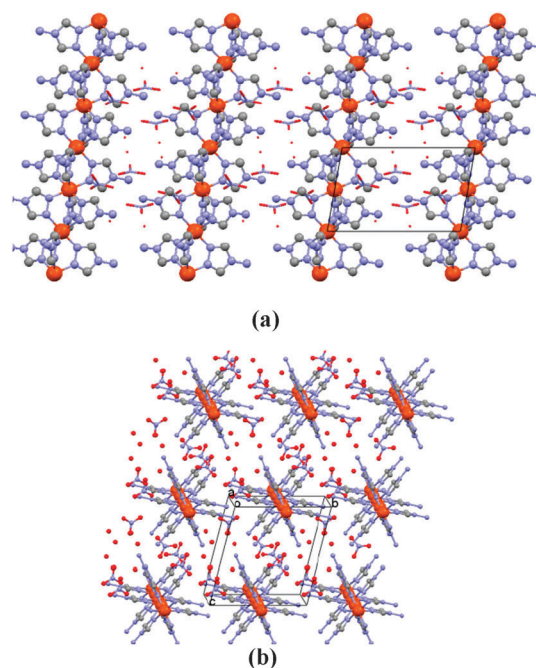
**Fig. 1** A view of the asymmetric unit in single crystals of  $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  at 120 K. Centres of inversion are represented with grey spheres.

crystals are damaged during data collection. As a result, the final crystal structure† is of a low-level quality compared to modern standard single crystal investigations, but still represents the first single crystal data on  $[\text{Fe}(\text{Rtrz})_3]\text{X}_2 \cdot n\text{H}_2\text{O}$  spin crossover systems. Note that single crystals are destroyed when warming above room temperature in order to reach the high spin state, thus only the low spin crystal structure is presented here.

The solid crystallizes in the triclinic space group  $P\bar{1}$ . The crystal packing is formed on the basis of an asymmetric unit, which contains three  $\text{NH}_2\text{trz}$  ligands connecting two  $\text{Fe}(\text{II})$  centers, two  $\text{NO}_3^-$  anions and two water molecules on general positions. Since the two iron atoms are located on inversion centres, the formula of the crystal is then  $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (Fig. 1).

The two iron atoms, denoted Fe1 and Fe2, are located on adjacent centres of inversion along the  $a$  direction. As a result, iron atoms are aligned along the  $a$  direction and since they are linked by the  $\text{NH}_2\text{trz}$  ligands, infinite chains of the  $a$  axis are formed. The 1-D polymeric nature of these materials is thus definitively confirmed (Fig. 2). Another consequence of the special position adopted by the iron atoms is that all neighbouring intrachain Fe centres are separated by a distance of half the  $a$  unit cell parameter, *i.e.*  $3.655(3)$  Å. It is well-known that the geometry of the metal coordination sphere directly reflects the spin state of the metal ion.<sup>12</sup> The Fe–N distances of the two iron sites clearly show that both iron ions are in low spin. The average Fe–N distances,  $\langle \text{Fe1–N} \rangle = 1.95(2)$  Å and  $\langle \text{Fe2–N} \rangle = 1.99(2)$  Å, indeed match the expected values for an almost full low spin state. The distortion of the coordination sphere, estimated through the so called sigma parameter,<sup>12</sup> demonstrates exceptionally low values,  $\Sigma = 15(1)^\circ$  and  $\Sigma = 11(1)^\circ$  for  $\text{Fe1N}_6$  and  $\text{Fe2N}_6$ , respectively. Such a weak distortion shows that the  $\text{FeN}_6$  coordination sphere is very close to a perfect octahedron in the case of  $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , which is contrary to what is generally observed in spin crossover materials, where values can be 3–5 orders of magnitude superior to the present data. This is probably one of the peculiar properties of the 1-D polymeric spin crossover materials, that they constrain iron to adopt rigid and regular coordination spheres. The relatively low quality of the present crystal structure refinement, compared to an actual standard single crystal structure refinement, does not allow further comment on the apparent small differences between the Fe1 and Fe2 coordination sphere geometries.

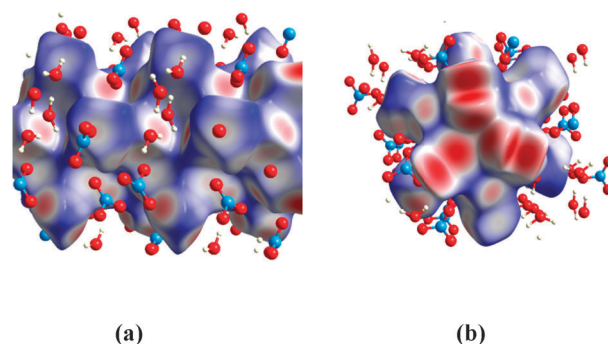
Certainly one of the most important points brought by the present result is to allow the description of the crystal packing in such a kind of spin crossover material. In this respect, it is



**Fig. 2** A view of the chains within the crystal packing in  $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , (a) along  $b$  and (b) along  $a^*$ . H atoms are omitted for clarity.

evident that the chains are far apart to be isolated from each other. First, anions and water molecules participate in the crystal cohesion and draw intermolecular interactions through hydrogen bonding with the chains. Normalized intermolecular contacts mapped on the Hirshfeld surfaces (Fig. 3) of one chain illustrate the insertion of anions and water into the cavity of the chains. Anions and water molecules weave a dense interaction network linking all of the chains. Water molecules for instance show short distances with  $\text{NH}_2$  terminal group. Furthermore, a same  $\text{NO}_3^-$  anion interacts simultaneously with two adjacent chains. Second,  $\text{NH}_2$  terminal group makes hydrogen bond with  $\text{trz}$  of adjacent chains along  $b$ .

This result proves the feasibility of obtaining single crystals of polymeric  $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  material, likewise in



**Fig. 3** Normalized intermolecular contacts mapped on the Hirshfeld surfaces of a chain in  $[\text{Fe}(\text{NH}_2\text{trz})_3](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  at 120 K showing the interaction between the chain and the anions and water molecules. (a) A view perpendicular to the chain axis and (b) along the chain axis. The colour scale describes the distances longer (blue), equal (white) or shorter (red) than the van der Waals radii. This figure was produced using Crystal Explorer.<sup>13</sup>

a very simple manner and soft experimental conditions. Efforts are currently performed to obtain larger single crystals allowing further and more accurate investigations of these materials. The present study also represents the first single crystal based structural data on the spin crossover material family,  $[\text{Fe}(\text{Rtrz})_3]\text{X}_2 \cdot n(\text{solvent})$ , which satisfied some of the requirements imposed for application, like the occurrence of spin crossover regime around room temperature.<sup>5a,6,14</sup> The 1-D polymeric construction through infinite  $(\text{Fe}(\text{Rtrz})_3)_n$  chains is definitively established. The crystal structure reveals that the crystal cohesion is formed from a dense interchain interaction network. Such a feature must be taken into account in the subsequent description of the physical properties of this family of materials, since the density of intermolecular interactions has been proven to be directly connected to the spin transition features in general.<sup>12,15</sup> Moreover, the strong involvement of the water molecule within the crystal cohesion shown by the present study enhances the potential role of the water molecules on the physical properties of the  $[\text{Fe}(\text{Rtrz})_3](\text{anion})_2 \cdot n\text{H}_2\text{O}$  spin crossover materials.

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## Notes and references

‡  $\text{C}_6\text{H}_{16}\text{FeN}_{14}\text{O}_8$ .  $M = 468.18 \text{ g mol}^{-1}$ . Crystal structure at 120 K, triclinic  $P\bar{1}$  space group,  $Z = 2$ ,  $a = 7.311(5) \text{ \AA}$ ,  $b = 10.562(5) \text{ \AA}$ ,  $c = 11.340(1) \text{ \AA}$ ,  $\alpha = 103.765(5)^\circ$ ,  $\beta = 98.10(1)^\circ$ ,  $\gamma = 95.52(1)^\circ$ ,  $V = 834.3(8) \text{ \AA}^3$ . 1187 collected reflections, 696 unique and 504 observed,  $R_{\text{int}} = 0.062$ , 136 refined parameters, refinement on  $F^2$ ,  $R_{\text{obs}} = 0.0938$ ,  $wR_{2\text{obs}} = 0.2342$ ,  $S = 1.03$ . Very weak diffraction pattern and damages to the crystal due to the X-ray beam prevented us from getting a usual intensities/parameters to refined ratio. The crystal structure has been solved by direct methods with SHELXS and refined by full matrix least-squares methods using SHELXL<sup>16</sup> in the WingX environment<sup>17</sup>. The weak number of observed intensities only allowed a refinement based on isotropic thermal parameters. CCDC 833475. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc14220h

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