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### COMMUNICATION

# Incorporation of spin-5/2 chain into 2D network with conformational pure *e,a-cis*-cyclohexane-1,4-dicarboxylato linker<sup>†</sup><sup>‡</sup>

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A two-dimensional coordination network,  $^2_{\infty}$ [Fe<sup>III</sup> (OH)(*e*,*acis*-1,4-chdc)] (1,4-chdc: cyclohexane-1,4-dicarboxylate), featuring one-dimensional iron(III)-hydroxy chains that are transversely bridged by 1,4-chdc in its pure *e*,*a*-*cis* conformation have been isolated. The magnetic study shows a typical spin-5/2 Heisenberg chain above 20 K, but canted antiferromagnetic ordering at lower temperatures.

One-dimensional (1D) magnetic chains attract lots of research interest in that many intriguing quantum phenomena such as spin-Peierls transitions, Haldane gaps and tunnelling effects were observed experimentally or theoretically in recent years.<sup>1</sup> Among these materials many of them are "regular magnets" with equal dimensions of structure and magnetism. In fact, higher-dimensional structures can effectively contain magnetic behaviour with low-dimensional characteristics. This phenomenon has been emerging in the field of magnetic metal–organic frameworks (MMOFs),<sup>2</sup> in which typical low-dimensional magnetism such as slow-relaxation of single-molecule and single-chain magnets have been observed.<sup>3,4</sup>

We have been endeavouring to obtain low-dimensional magnetism with MMOFs since 2006 when we successfully obtained a single-chain magnet (SCM) by assembling an Ising-type  $[-Co-(OCO)_4-Co-]_n$  chain into a 2D coordination network with the *trans*-cyclohexane-1,2-dicarboxylato bridge.<sup>5</sup> Later on, we expanded this method to other dicarboxylato systems with different metal centres such as Ni(II), Fe(II) and mixed-valent Fe(II)-Fe(III).<sup>6</sup> Most of these materials exhibit dynamic magnetism related to the SCM behaviour, but being disturbed by peripheral magnetic contacts.<sup>7</sup>

As part of our on-going exploration of 1D magnetism in MMOFs we report here a unique iron( $\Pi$ )-hydroxy chain trapped into a 2D network by a *e,a-cis*-cyclohexane-1,4-dicarboxylate (*e,a-cis*-1,4-chdc) bridge. The resulting compound,

 ${}_{\infty}^{2}$  [Fe<sup>III</sup>( $\mu$ -OH)(*e*,*a*-*cis*-1,4-chdc)] (1), magnetically behaves as a typical spin-5/2 Heisenberg chain above 20 K. Below this temperature, long-range canted antiferromagnetic ordering was developed.

We prepared 1 from a conformational mixture of 1,4-chdcH<sub>2</sub>, FeCl<sub>3</sub>, NaOH at a molecular ratio of 1:1:1:1.5 and relatively mild hydrothermal conditions (160 °C for 2 days). The resulting pure *e,a-cis* conformation of 1,4-chdc in 1 is somehow, not surprising because in the three conformations of 1,4-chdcH<sub>2</sub>, namely *a,a-trans*, *e,e-trans*, and *e,a-cis* the *e,a-cis* conformation is the thermodynamically medium stable form, but only 1.4 kcal mol<sup>-1</sup> above the most stable *e,e-trans* form, as shown in Fig. 1. Therefore, most of the conformations of 1,4-chdc in solid states adopt either the *e,e-trans* or *e,a-cis* forms, <sup>8,9</sup> and only very few cases of *a,a-trans* conformation are known.<sup>10</sup>

We have been able to isolate the conformational pure *e,e-trans* form of 1,4-chdc in a mixed-valent iron(II,III) compound, [Fe<sup>II</sup>-Fe<sup>III</sup>( $\mu_4$ -O)(*e,e-trans*-1,4-chdc)\_{1.5}]\_{\infty} (**2**), at higher temperature hydrothermal conditions (220 °C for 3 days).<sup>6d</sup> Therefore, with both **1** and **2** the story of conformation separation by differentiating synthetic temperature is now complete, that is, higher temperature leads to the most stable *e,e-trans* product whereas lower temperatures prefer a less stable *e,a-cis* conformation. A similar story can be found in cadmium products reported by Cao *et al.*<sup>8b</sup>

In fact, the maximum Gibbs free energy difference between the conformations of 1,4-chdc is only 2.8 kcal mol<sup>-1</sup>, a value that is comparable to several types of supramolecular interactions such as hydrogen bonding,  $\pi$ – $\pi$  stacking and metallophilicity.<sup>12</sup> Once other peripheral factors are competing with the free energy the resulting conformations are hardly predicted, depending largely on a kinetic process. Therefore, many solid-state structures of 1,4-chdc comprise not just a single conformation but a mixture of *cis*- and *trans*-1,4-chdc, instead.<sup>8,9</sup> This phenomenon has also been observed extensively in other cyclohexanecarboxylate derivatives.<sup>13</sup>

<sup>‡</sup>Electronic supplementary information (ESI) available: Experimental details and additional magnetic data. CCDC 892309. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt31613g



Fig. 1 Equilibria between the three conformations of 1,4-chdc. The Gibbs free energy difference  $\Delta G$  values are compared to the *e,e-trans* form.<sup>11</sup>

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The solid-state structure of 1 features layers (Fig. 2a) with alternating iron(III)-hydroxy chains and *e,a-cis*-1,4-chdc linkers. The compound condensed in the monoclinic space group  $P2_1/m$ . Interestingly, the coordination geometry of the iron(III) ion is in a compressed octahedron with two shorter axial oxygen vertexes (Fe–O 1.956(2) Å) from the hydroxy groups and four carboxylato-O atoms forming the equatorial plane with longer Fe-O bond distance of av. 2.015(2) Å. Each iron(III) centre sits exactly on the inversion centre, reflecting the "L"-shaped e,a-cis-1,4chdc ligand to other side. The two symmetry-equivalent e,a-cis-1.4-chdcs coordinate to the iron(III) ions in a head-to-head fashion like a "r-J" shape. In this arrangement the adjacent e,a-cis-1,4-chdc ligands along the crystallographic§ b-direction are not parallel, but facing each other. Similar situation occurs to other parts of the structure running along the *b*-axis, *i.e.* the hydroxide groups in the  $[-Fe(III)-OH-]_n$  chain are undulating around the central iron(III) ions (Fe-O-Fe 123.4(2)°). Note that the single-arm hydroxide indicates the adjacent iron(III) ions are not central-symmetry related. The intrachain Fe---Fe separation is 3.444 Å and the shortest interchain Fe---Fe distance is 8.569 Å. These laminated layers are further stacked along the *a*-axis with a shortest interlayer Fe…Fe distance of 8.010 Å (Fig. 2b).

The magnetic properties of **1** (Fig. 3) reflect the 1D  $[-\text{Fe}(\text{III})-OH-]_n$  chain at higher temperatures. The  $\chi T$  product exhibits a continuous decrease upon cooling to yield  $\chi T = 2.67 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at room temperature, a value much lower than the spin-only value (4.38 cm<sup>3</sup> mol<sup>-1</sup> K) of the iron(III)-ion with half-filled 3d orbitals, indicating strong antiferromagnetic interactions within the chain.

Since the basic magnetic unit is represented by the *syn–syn* carboxylato-bridged  $[-Fe(III)-OH-]_n$  chain and the magnetic anisotropy of the high-spin d<sup>5</sup> ions are virtually negligible, the magnetic properties of the Fe(III) spin-5/2 chain in **1** were modeled using the Hamiltonian in eqn (1),

$$\hat{H} = -J \sum_{-\infty}^{+\infty} \vec{S}_i \vec{S}_{i+1} \tag{1}$$

which can be solved by the classical Fisher model,  $^{14}$  resulting in eqn (2),

$$\chi_{\text{chain}} = \frac{N(M\beta)^2}{3k_{\text{B}}T} \frac{(1-u)}{(1+u)}$$
(2)

where  $M = g[S(S + 1)]^{1/2}$  and  $u = \operatorname{coth}(J/k_{\rm B}T) - k_{\rm B}T/J$ . In the classical spin limit, the exchange energy *J* must be scaled following the usual procedure:  $J \rightarrow JS(S + 1)$ . A best fit between 20 and 320 K using eqn (2) results in  $J = -21.4(2) \text{ cm}^{-1}$ , g = 2.05(1) and  $R = 4.7 \times 10^{-5}$ , where  $R = \Sigma[(\chi_{\rm obs} - \chi_{\rm cal})/(\chi_{\rm obs})]^2$  indicates the fit quality. The large negative value *J* corresponds to strong antiferromagnetic interactions through the hydroxy *syn*-*syn* carboxylato bridge and the Landé g-factor close to a value of 2 indicates a fairly isotropic magnetism, further confirming the justifiability of using the Heisenberg fitting model.



**Fig. 3** Upper: temperature dependence of  $\chi T$  and  $\chi_m$  (inset) of 1, referred to one Fe(III) ion, at indicated applied fields. Red line: fitting result using eqn (2). Lower: hysteresis loop of 1 measured at 1.9 K.



Fig. 2 The layered structure (a) and the crystal packing comprising two layers (b) in 1. Colour codes: iron, green; oxygen, red and carbon, light grey.

Below 20 K, a kink was observed in the  $\chi T$  product, which is a typical signal of the non-diamagnetic ground state. To further elucidate this phenomenon the field-cooled magnetisation at different external fields was measured, see the inset of Fig. 3. The molar susceptibility curve at lower fields show a ramp below 7 K, reaching a maximum of 0.5 cm<sup>3</sup> mol<sup>-1</sup> at 2 K. The onset of a sharp increase at lower fields referred to a spin-canted antiferromagnetism with long-range ordering, which was further confirmed by the ac susceptibility data (Fig. S1‡). Both in-phase and out-of-phase ac susceptibility peak at 3.2 K without any frequency-dependent behaviour.

Moreover, a hysteresis loop was clearly recorded at 1.9 K with a coercive field of 110 Oe and a remnant magnetisation ( $M_R$ ) of 0.04  $\mu_B$  (Fig. 3), showing the typical behaviour of a weak ferromagnet. The linear increase of the *M* vs. *H* plot at higher fields without saturation confirms this behaviour (Fig. S2<sup>+</sup><sub>4</sub>). The equation,  $\tan \alpha = M_R/M_S$ , was therefore used to measure the canting angle  $\alpha$  by taking  $M_S = gS = 5 \mu_B$ . The resulting  $\alpha =$ 0.5° indicates a very small canting angle between two spin orientations. Compared to the Fe–O<sub>hydroxy</sub>–Fe bond angle  $\alpha$  does not suggest a collinear alignment of the bond direction and the principle magnetic axis.

Indeed, the isotropic nature of the iron(III) ion does not favour the spin-canting behaviour originated from the Dzialoshinski– Moriya (DM) interaction,<sup>15</sup> which tends to orientate the parallel spins into a perpendicular fashion. Without a significant magnetic anisotropy the occurrence of the canted antiferromagnetism mainly due to the lack of inversion-centre between the adjacent iron(III) ions. The asymmetric hydroxy-carboxylato bridge between the nearing metal centres contributes the main source of DM interaction.

Bearing a net magnetic moment from spin-canting does not necessarily lead to long-range collective behaviour. The presence of the magnetic ordering in 1 suggests that some superexchange-coupling interaction propagating through the chemical bonds does exist regardless of the far separation of the chains. We took the risk of over-parameters to extract this interchain magnetic interaction by appending a mean-field approximation term to eqn (2):  $\chi = \chi_{chain}/(1 - zJ'\chi_{chain}/Ng^2\mu_B^2)$ , where zJ' accounts for the interchain magnetic interaction. The best fitting between 20 and 320 K leads to  $J = -20.3(2) \text{ cm}^{-1}$ ,  $zJ' = -1.1(2) \text{ cm}^{-1}$ , g = 2.16(1) and  $R = 6.8 \times 10^{-6}$ . Interestingly, the quantity of the zJ' agrees well with the reported value of an *e,e-trans*-1,4-chdc bridge between two titanium(III) ions,<sup>16</sup> indicating a potential superexchange-coupling pathway through the  $\sigma$ -bonds.

In summary, by using mild hydrothermal synthesis the pure e,a-cis conformation of the 1,4-chdc ligand can be integrated into a 2D coordination polymer, linking a novel iron(III)-hydroxy chain with spin-canted antiferromagnetism. We postulate that the  $\sigma$ -bonding is the primary superexchange-coupling pathway of weak inter-chain magnetic interactions, which leads to the establishment of long-range magnetic ordering below 4 K.

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§ Crystal data for 1: C<sub>8</sub>H<sub>22</sub>FeO<sub>5</sub>, M = 234.02, monoclinic, space group  $P2_1/m$  (No. 11), a = 8.010(2), b = 6.8872(18), c = 8.569(2) Å,  $\beta = 108.232(5)^\circ$ , V = 449.0(2) Å<sup>3</sup>, Z = 2,  $D_c = 1.797$  g cm<sup>-3</sup>, Mo K<sub>a</sub> ( $\lambda = 0.71073$  Å). Completeness = 99.2% (to  $\theta_{max} = 27^\circ$ ), T = 223(2) K, total reflections: 2447, unique reflections: 1054,  $\mu = 1.671$  mm<sup>-1</sup>, 76 parameters,  $R_1 = 0.0380$  ( $I > 2\sigma$ ),  $wR_2 = 0.895$  (all data) and S = 1.038. Bruker SMART Apex CCD diffractometer. The structure was solved by direct methods and all non-H atoms were subjected to anisotropic refinement on  $F^2$  using SHELXTL.

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