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## Support Information for

# Magnetite-like Mixed-Valence Iron Ferrimagnetic Homohelical Chains Exhibiting Spin Canting, Spin-Flop and Field Induced SCMs Like Behaviours

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#### **Experimental Section**

**Synthesis:** 1 and 2,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0.55 g) in formic acid, diethanolamine and N,N'-Diethyl-1,3propanediamine 12 mL (V/V/V = 8:3:0.8) sealed in a Teflon-lined stainless steel vessel, heated at 140 °C (for 1) and 80 °C (for 2) for 2 days under autogenous pressure, and then cooled to room temperature. Red and black crystals of 1 and 2 were harvested in about ~30% yield based on FeCl<sub>3</sub>·6H<sub>2</sub>O. Anal. Calcd of 1 for C<sub>6</sub>H<sub>8</sub>Fe<sub>3</sub>O<sub>14</sub>: C, 15.28; H, 1.71; Found: C, 15.32; H,1.68 %. Anal. Calcd of 2 for C<sub>8</sub>H<sub>13</sub>Fe<sub>3</sub>O<sub>19</sub> : C, 16.55; H, 2.26; Found: C, 16.36; H,2.05 %.

<sup>§</sup>Crystal data for 1, C<sub>6</sub>H<sub>8</sub>Fe<sub>3</sub>O<sub>14</sub>: M = 471.67, trigonal,  $P3_22I$ , a = b = 10.4091(12) Å, c = 11.015(2) Å, V = 1033.6(3) Å<sup>3</sup>, Z = 3, Dc = 2.273 Mg/m<sup>3</sup>,  $\mu = 3.193$  mm<sup>-1</sup> 2204 reflections [R(int) = 0.0418] of which 1269 assumed as observed ( $I > 2\sigma(I)$ ), final  $R_I = 0.0701$ ,  $wR_I = 0.1531$  ( $I > 2\sigma(I)$ ), flack = 0.08(4).

Crystal data for **2**,  $C_8H_{13}Fe_3O_{19}$ : M = 580.73, Monoclinic, Cc, a = 17.062(3) Å, b = 6.8226(15) Å, c = 16.186(4) Å,  $\beta = 100.84(2)^\circ$ , V = 1850.6(7) Å<sub>3</sub>, Z = 4, Dc = 2.084 Mg/m<sup>3</sup>,  $\mu = 2.418$  mm<sup>-1</sup> 1845 reflections [R(int) = 0.0632] of which 1477 assumed as observed ( $I > 2\sigma(I)$ ), final  $R_I = 0.0545$ ,  $wR_I = 0.1192$  ( $I > 2\sigma(I)$ ), flack = -0.04(6).

**Materials and methods.** All chemicals were reagent grade and used as purchased without further purification. The XRPD spectra were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Simulation of the XRPD spectrum were carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge via the internet at <u>http://www.iucr.org</u>. The Mössbauer spectrum was performed using a conventional Mössbauer spectrometer (American Fast Com Tec Pc-moss II). Magnetic susceptibility was measured by a Quantum Design MPMS superconducting quantum interference device (SQUID). Diamagnetic corrections were estimated by using Pascal constants and background corrections by experimental measurement on sample holders.

**X-ray Crystallography.** The single-crystal X-ray diffraction data of 1 and 2 were collected on a Rigaku SCX-mini diffractometer at 293 (2) K with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) by  $\omega$  scan mode. The program *CrystalClear<sup>SI</sup>* was used for the integration of the diffraction profiles. The structure was solved by direct method using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL (semi-empirical absorption corrections were applied by using the SADABS program).<sup>82</sup> The non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on  $F^2$ . All hydrogen atoms of were generated theoretically at the specific atoms and refined isotropically with fixed thermal factors. The selected bond lengths and angles are given in Tables S1.

#### References

- S1. G. M. Sheldrick, *SHELXL97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.
- S2. CrystalClear and CrystalStructure; Rigaku/MSC: The Woodlands, TX, 2005.

		1	
Fe1—O15 <sup>i</sup>	2.082 (12)	Fe2—O10	2.026 (12)
Fe1—O1	1.927 (11)	Fe2—O1	1.918 (11)
Fe1—O8	2.031 (12)	Fe2—O4	2.031 (12)
Fe1—O5	2.016 (12)	Fe3—O7	2.017 (13)
Fe1—O6	2.045 (13)	Fe3—O1	1.925 (11)
Fe1—O3	2.017 (11)	Fe3—000B	2.101 (11)
Fe2—O14	2.089 (11)	Fe3—O11	2.022 (12)
Fe2—O12	2.046 (12)	Fe3—O9	2.031 (13)
Fe2—O2	2.048 (11)	Fe3—O13	2.036 (15)
Fe2—O1—Fe1	119.3 (5)	Fe3—O1—Fe1	119.8 (5)

 Table S1. Selected bond lengths [Å] and angle [°] for 1 and 2.

Fe2—O1—Fe3	120.8 (6)						
Symmetry codes: (i) $x+1/2$ , $y-1/2$ .							
2							
Fe1—O7	1.914 (4)	Fe2—O6 <sup>i</sup>	2.051 (7)				
Fe1—O1	2.130 (6)	Fe2—O6	2.051 (7)				
Fe1—O2 <sup>i</sup>	2.136 (6)	Fe2—O7	1.863 (8)				
Fe1—O2 <sup>ii</sup>	2.183 (6)	Fe2—O1W	2.024 (10)				
Fe1—O5	2.030 (7)	Fe2—O4	2.040 (7)				
Fe1—O3	2.043 (7)	Fe2—O4 <sup>i</sup>	2.040 (7)				
Fe1 <sup>i</sup> —O2—Fe1 <sup>iii</sup>	106.1 (3)	Fe2—O7—Fe1	118.8 (2)				
Fe1 <sup>i</sup> —O7—Fe1	122.5 (4)	Fe2—O7—Fe1 <sup>i</sup>	118.8 (2)				
Symmetry codes: (i) $y, x, -z+1$ ; (ii) $-y+2, x-y+1, z-1/3$ ; (iii) $-x+y+1, -x+2, z+1/3$ .							

### Table S2. Mössbauer Parameters for 1.

	Doublet (1) $/\text{Fe}^{3+}$			Doublet(2)/Fe <sup>2.5+/2+</sup>				
		ISOMER	Q.	LINE		ISOMER	Q.	LINE
T (K)	Area	SHIFT	SPLITTING	WIDTH	Area	SHIFT	SPLITTING	WIDTH
300	37.90%	0. 42	0.97	0.27	62.10%	0.80	0.41	0.24
230	31.30%	0.56	1.17	0.29	68.70%	0.80	0.41	0.36
120	23.90%	0.70	1.31	0.36	76.10%	0.79	0.54	0.58
50	69.40%	0.54	1.11	0.43	30.60%	1.37	2.48	0.39
30	67.40%	0. 58	1.02	0.41	32.60%	1.26	2.67	0.35



Fig. S1 Polyhedron view of the polymeric chain in 1.



Fig. S2 UV-Vis spectrum of 1 (red) and 2 (black) in solid state.



Fig. S3 The XRPD patterns of complexes 1 and 2.



Fig. S4  $\chi_M^{-1}$ vsT Plots of 2 the red solid lines are the fitting by the Curie–Weiss law.



**Fig. S5**  $M/N \mu_{\rm B}$  vs H plots of 1 and 2.

As shown in Fig.4a, at room temperature, the  $\chi_M T$  of **2** have a values 4.31 cm<sup>3</sup> mol<sup>-1</sup>, which values are much smaller than the spin value expected for three high-spin Fe<sup>3+</sup> ions. The magnetization at 2 K also suggests strong antiferromagnetic interactions in 2, which increase linearly with that of the field and reaches 0.36 N $\beta$  at 5 T far from the saturated value (Fig. S5). The magnetic data above 35 K of **2** was

fitted by isotropic Heisenberg spin Hamiltonian with  $C_3$  symmetry  $H = -2J(S_1S_2 + S_2S_3 + S_3S_1)$  in which  $S_1 = S_2 = S_3 = 5/2$ . And the equation is

$$\chi_{t} = \frac{Ng^{2}\beta^{2}}{3kT} \times \frac{3+60e^{3J/kT}+315e^{8J/kT}+630e^{15J/kT}+990e^{24J/kT}+1287e^{35J/kT}+1365e^{48J/kT}+1020^{e63J/kT}}{4+16e^{3J/kT}+36e^{8J/kT}+40e^{15J/kT}+40e^{24J/kT}+36e^{35J/kT}+28e^{48J/kT}+16^{e63J/kT}} = \frac{Ng^{2}\beta^{2}}{4kT} \times \frac{1+20e^{3J/kT}+105e^{8J/kT}+210e^{15J/kT}+330e^{24J/kT}+429e^{35J/kT}+455e^{48J/kT}+340e^{63J/kT}}{1+4e^{3J/kT}+9e^{8J/kT}+10e^{15J/kT}+10e^{24J/kT}+9e^{35J/kT}+7e^{48J/kT}+4e^{63J/kT}}$$

$$\chi_M = \frac{\chi t}{1 - (2zj'/Ng^2\beta^2)\chi_t}$$



**Fig. S6** The  $ln(\chi_M T)$  vs. 1/T plot of 1 under 0.1T, the red solid line represents the fit to the Ising model.



**Fig. S7** Frequency dependence of the  $\chi \square_m$  and  $\chi \square_m$  in a 0.1T dc field (above) for 1 at 2.7-1.8 K.



Fig. S8 The ac susceptibility of 1 in 2-10 K under dc field 0.2 T.



**Fig. S9** Peak temperatures of  $\chi \square_m$  fitted by Arrhenius law.