A cyano-bridged tubular coordination polymer with dominant ferromagnetic interactions

Peng-Fei Zhuang, Tao Liu,* Xian-Hui Xie, Cheng He, and Chun-Ying Duan

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, 116024, China

E-mail address: liutao@dlut.edu.cn; Tel: +86-411-84986316; fax: +86-411-84986314.

Synthesis of 1: A 3.0 mL aqueous solution of $K_2[Fe^{II}(bipy)(CN)_4]\cdot 3H_2O$ (0.05 mmol) was placed at the bottom in one side of an H-shaped tube, and a 3.0 mL aqueous solution of $Mn(ClO_4)_2\cdot 6H_2O$ (0.05 mmol) was introduced into the other side. Then, 12 mL of water was layered over the solutions on both sides to provide a diffusion pathway. Four or five weeks later, red crystals appeared and were collected and dried in air after quickly being washed with water. Yield: 46% based on $Mn(ClO_4)_2\cdot 6H_2O$. Anal. calcd (%) for $C_{14}H_{12}MnFeN_6O_2$: C, 41.31; H, 2.97; N, 20.65; Found (%): C, 41.21; H, 2.85; N, 20.51. The dehydrated sample was obtained via heating the hydrated sample at 120°C for 12 hours.

Crystal structure analysis: The data were collected at a temperature of 296 ± 2 K on a Bruker Smart APEX II X–diffractometer equipped with graphite monochromated Mo–Kα radiation (λ = 0.71073 Å) using the SMART and SAINT programs. The structure was solved in the space group *P*−1 by direct method and refined by the full–matrix least–squares fitting on F^2 using SHELXTL.[S1]All non–hydrogen atoms were treated anisotropically. Hydrogen atoms of organic ligands were generated geometrically, Hydrogen atoms of O1 were added by difference Fourier maps. All hydrogen atoms were refined by a riding model.

[S1]: (a) Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122; (b) Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

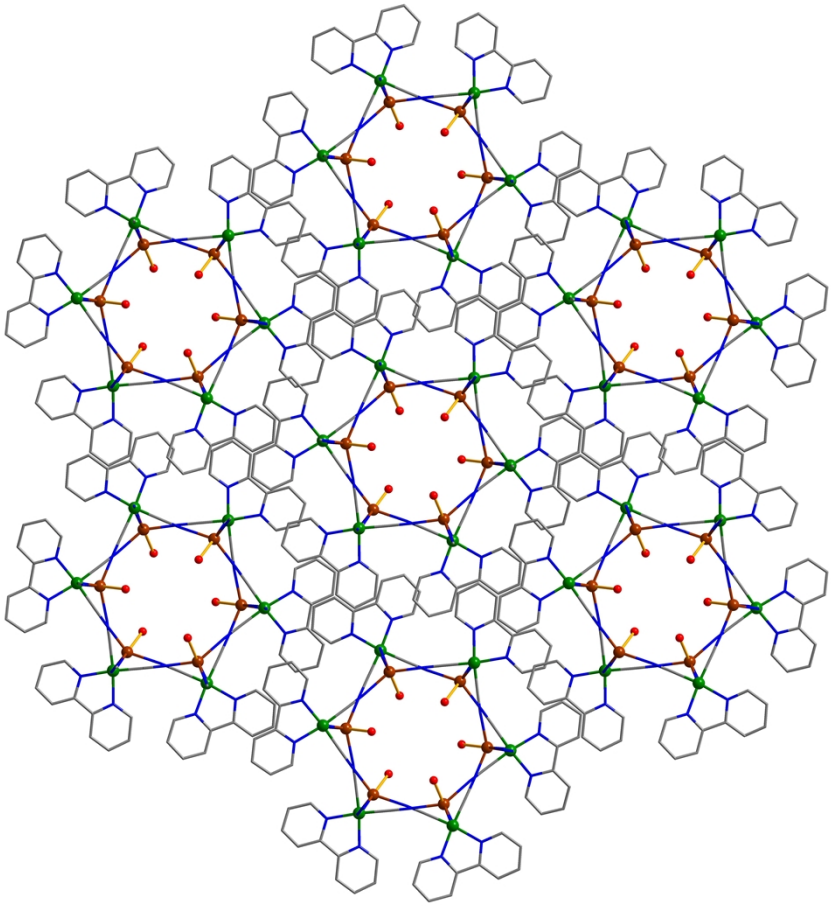

Figure S1 Packing diagram of **1** in the *ab* plane. H and O atoms are omitted for clarity (Fe green, Mn brown, C gray, N blue).

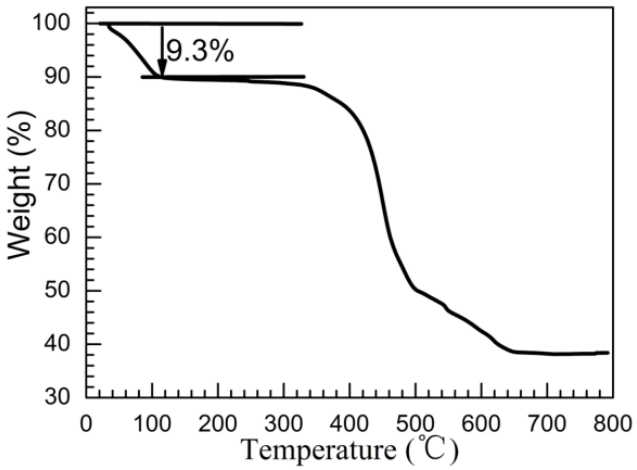

Figure S2 Thermal gravimetric analyses of **1** under a N_2 atmosphere.

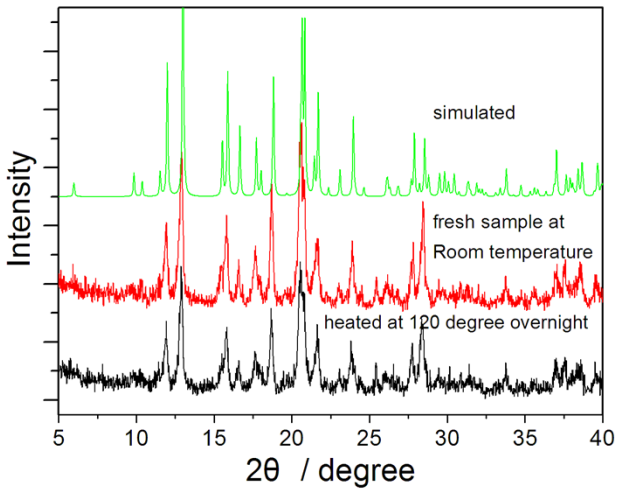

Figure S3 The experimental powder XRD pattern and the simulated XRD pattern of **1**.

Table S1 Selected bond lengths (Å) and angles (º) for **1**.

Complex **1**			
Fe(1)-C(12)	1.887(4)	Mn(2)-N(5)#1	2.115(4)
Fe(1)-C(13)	1.886(4)	Mn(2)-N(4)#2	2.122(4)
Fe(1)-C(11)	1.918(4)	Mn(2)-N(3)#3	2.143(3)
Fe(1)-C(14)	1.929(4)	Mn(2)-N(6)	2.166(3)
Fe(1)-N(2)	1.985(3)	Mn(2)-O(1)	2.363(3)
Fe(1)-N(1)	1.995(3)		
C(13)-Fe(1)-C(12)	90.72(17)	C(14)-Fe(1)-N(1)	92.70(14)
C(12)-Fe(1)-C(11)	91.59(15)	N(2)-Fe(1)-N(1)	80.08(14)
C(13)-Fe(1)-C(11)	90.67(16)	N(5)#1-Mn(2)-N(4)#2	143.52(16)
C(12)-Fe(1)-C(14)	86.03(15)	N(5)#1-Mn(2)-N(3)#3	92.33(13)
C(13)-Fe(1)-C(14)	86.66(15)	N(4)#2-Mn(2)-N(3)#3	90.78(13)
C(11)-Fe(1)-C(14)	176.39(16)	N(5)#1-Mn(2)-N(6)	104.54(14)
C(12)-Fe(1)-N(2)	93.92(15)	N(4)#2-Mn(2)-N(6)	108.62(13)
C(13)-Fe(1)-N(2)	175.37(16)	N(3)#3-Mn(2)-N(6)	109.33(13)
C(11)-Fe(1)-N(2)	89.23(13)	N(5)#1-Mn(2)-O(1)	84.58(13)
C(14)-Fe(1)-N(2)	93.63(13)	N(4)#2-Mn(2)-O(1)	84.20(12)
C(12)-Fe(1)-N(1)	173.78(16)	N(3)#3-Mn(2)-O(1)	166.72(13)
C(13)-Fe(1)-N(1)	95.29(17)	N(6)-Mn(2)-O(1)	83.95(12)
C(11)-Fe(1)-N(1)	89.95(14)		

[a] Symmetry transformations used to generate equivalent atoms for **1**: #1 x-y+1/3,x-1/3,-z+2/3; #2 y+1/3,-x+y+2/3,-z+2/3; #3 x,y,z-1.