

Supporting Information (SI)

A Spin-canted Polynuclear Manganese Complex Comprised of Alternating Linkage of Cyclic Tetra-and Mononuclear Fragments

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Experimental Section

Materials and methods.

All chemicals were of reagent grade and used as purchased without further purification.

Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C analyzer (Perkin-Elmer, USA). IR spectra were measured on a MAGNA-560 (Nicolet) FT-IR spectrometer with KBr pellets. Thermogravimetric (TG) analyses were carried out on a Rigaku standard TG-DTA analyzer with a heating rate of $10^{\circ}\text{C min}^{-1}$ from ambient temperature to 800°C under nitrogen gas. Powder X-ray diffraction (PXRD) spectra were recorded on a Bruker D8 FOCUS diffractometer with a Cu-target tube and a graphite monochromator. Simulation of the XRPD spectra 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 <http://www.iucr.org>. The magnetic measurements were performed by using an MPMS XL-5 SQUID magnetometer. Diamagnetic corrections were estimated by using Pascal constants and background corrections by experimental measurement on sample holders.

Synthesis of complex 1.

The ligand 1*H*-benzimidazole-2-carboxylic acid (H_2BIC) was prepared according to the method described in the literature.¹

A mixture of HBTA (0.060 g, 0.5 mmol), H_2BIC (0.081 g, 0.5 mmol), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.198 g, 1.0 mmol), EtOH (10 ml), and triethylamine (0.056 ml, 0.38 mmol) was sealed in a Teflon-lined autoclave, and heated to 140°C for 2 days then slowly cooled to 30°C in 12 h. Yield: *ca.* 10% with respect to HBTA. Element analysis (%): Calcd. for $\text{C}_{48}\text{H}_{41}\text{Mn}_6\text{N}_{24}\text{O}_4\text{Cl}_5$ (1524.89): C 37.81, H 2.71, N 22.05; found: C 38.05, H 2.53, N 22.38. IR (KBr pellets, cm^{-1}): 3394(s), 3081(w), 3050(m), 2724(w), 2647(m), 2478(m), 2346(w), 1610(m), 1573(m), 1484(m), 1446(s), 1394(m), 1263(s), 1189(vs), 1162(vs), 997(s), 919(s), 784(vs), 744(vs), 692(m), 636(s), 553(s).

Synthetic Discussion:

As illustrated in the introduction of this article, the reason for choosing HBTA is mainly attributed to the consideration that the tri-N-donor features of the triazolate group can provide more coordination sites for metal ions to form metal cluster building units, which has been demonstrated in recent publications. The mixed-ligand strategy has been well utilized to generate polynuclear complexes.² Our recent work has corroborated that the mixed-ligand strategy (HBTA and H₂BIC) is favorable to the construction of various cobalt-based cup-shaped building blocks (*CrystEngComm*, 2013, DOI:10.1039/C3CE42007H), however, the H₂BIC ligands are generated *in situ*. The successful synthesis of those cobalt-based building blocks enlightens us to conceive whether this strategy could be applied to other metal systems if the H₂BIC ligands were not generated *in situ*. Under the guidance of this strategy, luckily, the title complex (**1**) was prepared. Although the ligand H₂BIC does not exist in the final structures determined by single crystal X-ray diffraction, it may play an important role in the formation of **1** since **1** cannot be prepared under the absence of H₂BIC. Due to the solvothermal conditions, accurately assessing the role of H₂BIC in this system is beyond the scope of our abilities. Similar phenomena have also been observed in literature.^{2a, 3}

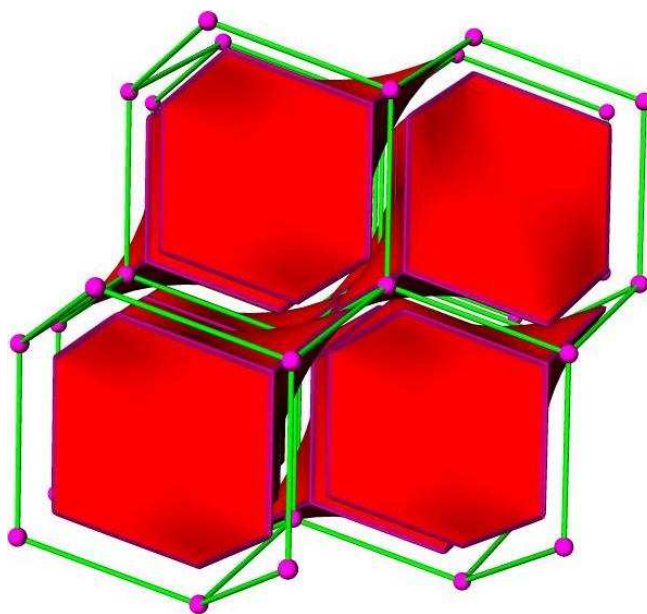
X-ray Crystallography.

The crystallographic data of **1** was collected on a Rigaku 007 Saturn 70 diffractometer at 113 K with Mo-K α radiation ($\lambda = 0.71073$ Å). The program *CrystalClear* was used for integration of the diffraction profiles. The crystal data was solved by direct methods and refined by a full-matrix least-square method on F^2 using the *SHELXL-97* crystallographic software package.⁴ All non-hydrogen atoms were refined anisotropically, and hydrogen atoms of the organic ligands

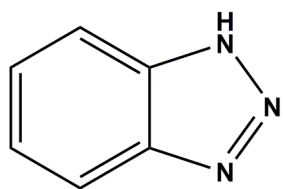
were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. Hydrogen atoms on water molecules can't be generated and were included in the molecular formula directly. Furthermore, the main framework of **1** is anionic. Considering the sources of cation and the acidic reaction environment in the formation of **1**, one H⁺ were directly included in the molecular formula to balance the negative charge. Similar cases are common in literature.⁵ Full crystallographic data for **1** has been deposited with the CCDC (958851). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Reference

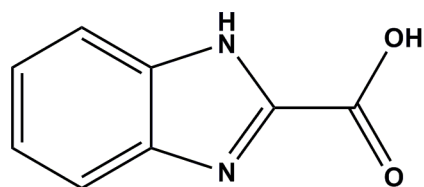
1. Xia, Z.; Wei, Q.; Yang, Q.; Qiao, C.; Chen, S.; Xie, G.; Zhang, G.; Zhou, C.; Gao, S. *CrystEngComm* **2013**, *15*, 86.
2. For examples, see: (a) Zheng, S.-T.; Wu, T.; Irfanoglu, B.; Zuo, F.; Feng, P.; Bu, X. *Angew. Chem., Int. Ed.* **2011**, *50*, 8034; (b) Tan, H.; Du, S.; Bi, Y.; Liao, W. *Chem. Commun.* **2013**, *49*, 8211; (c) Li, Y.-W.; Li, J.-R.; Wang, L.-F.; Zhou, B.-Y.; Chen, Q.; Bu, X.-H. *J. Mater. Chem. A* **2013**, *1*, 495; (d) Zheng, S.-T.; Bu, J. T.; Li, Y.; Wu, T.; Zuo, F.; Feng, P.; Bu, X. *J. Am. Chem. Soc.* **2010**, *132*, 17062.
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4. (a) Sheldrick, G. M. *SHELXL97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997; (b) Sheldrick, G. M. *SHELXS97, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.
5. (a) Duan, C.; Wei, M.; Guo, D.; He, C.; Meng, Q. *J. Am. Chem. Soc.* **2010**, *132*, 3321; (b) Wei, M.; He, C.; Hua, W.; Duan, C.; Li, S.; Meng, Q. *J. Am. Chem. Soc.* **2006**, *128*, 13318; (c) Zhang, H.; Lu, Y.; Zhang, Z.; Fu, H.; Li, Y.; Volkmer, D.; Denysenko, D.; Wang, E. *Chem. Commun.* **2012**, *48*, 7295.



Scheme S1. The tiling structure of **1**.

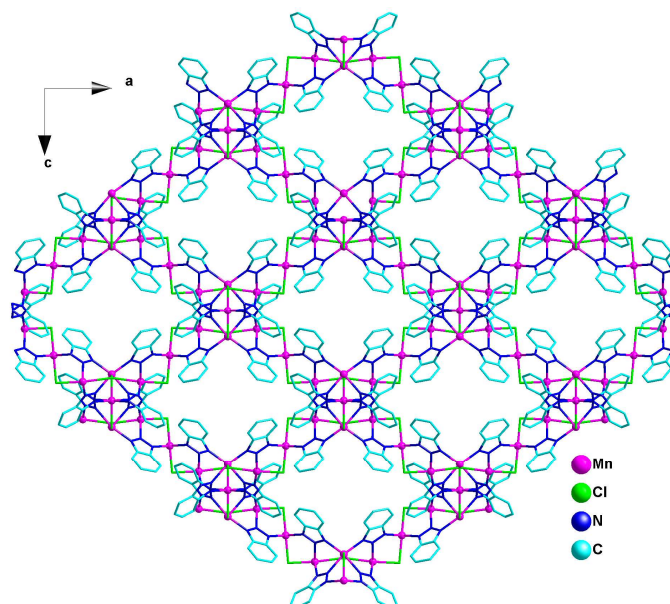


1H-Benzotriazole



1H-benzimidazole-2-carboxylic acid

Scheme S2. 1H-Benzotriazole (HBTA) and 1H-benzimidazole-2-carboxylic acid (H₂BIC).



Scheme S3. Ball-and-stick view of the 3D framework of **1** along the *b* axis (H atoms and solvent molecules are omitted for clarity).

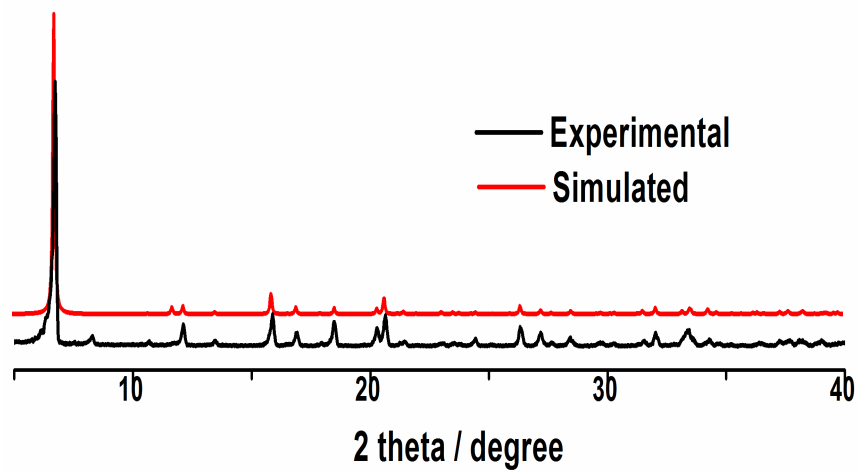


Figure S1. XRPD pattern of complex **1**.

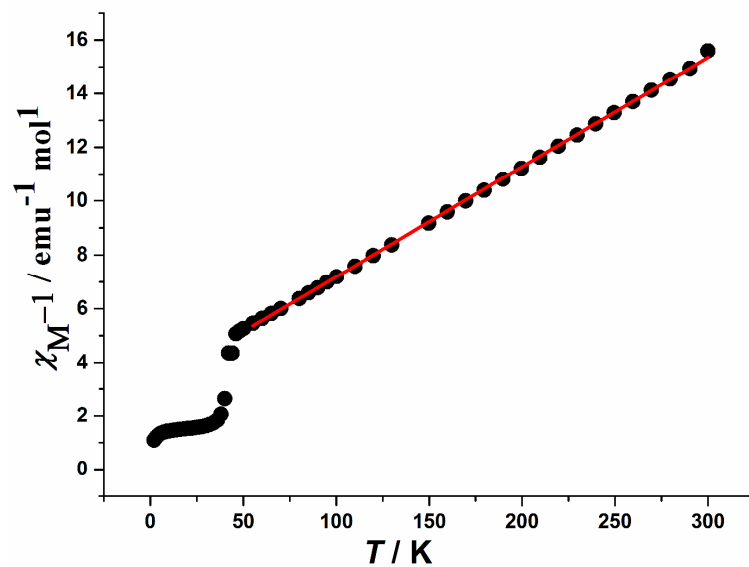


Figure S2. The Curie-Weiss plots of **1**. Solid line represents the best fit.

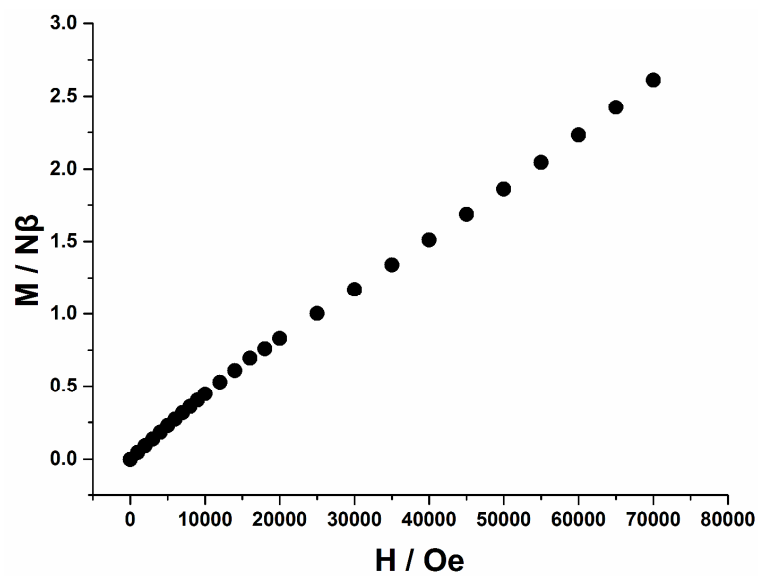


Figure S3. Field dependence of the magnetization (M) of **1** at 2 K.

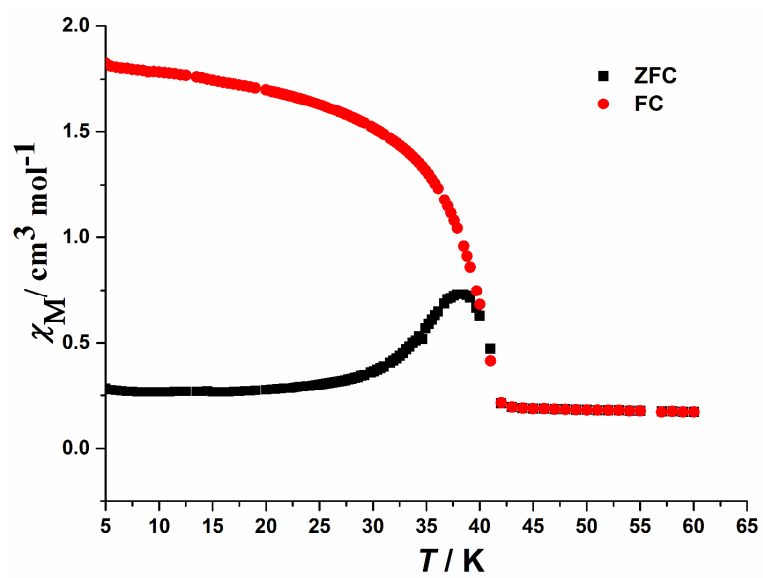


Figure S4. FC and ZFC magnetization of **1** in the dc field of 50 Oe.

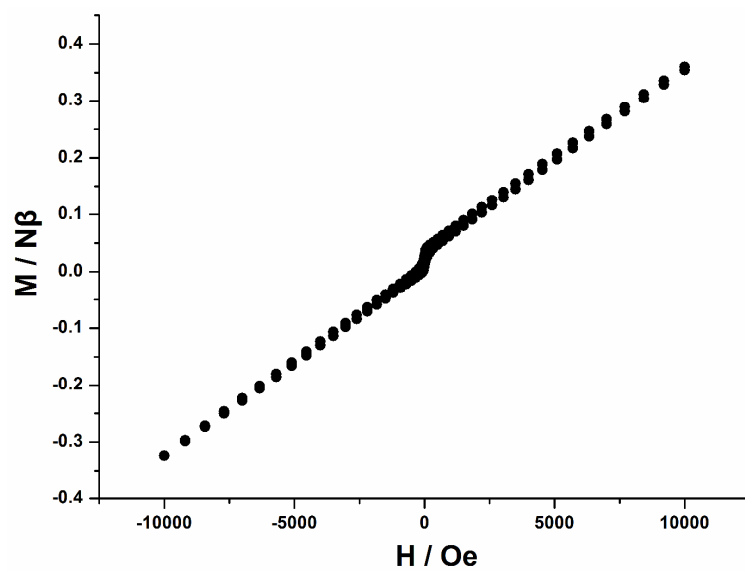


Figure S5. Plots of hysteresis loop of **1** at 2K.

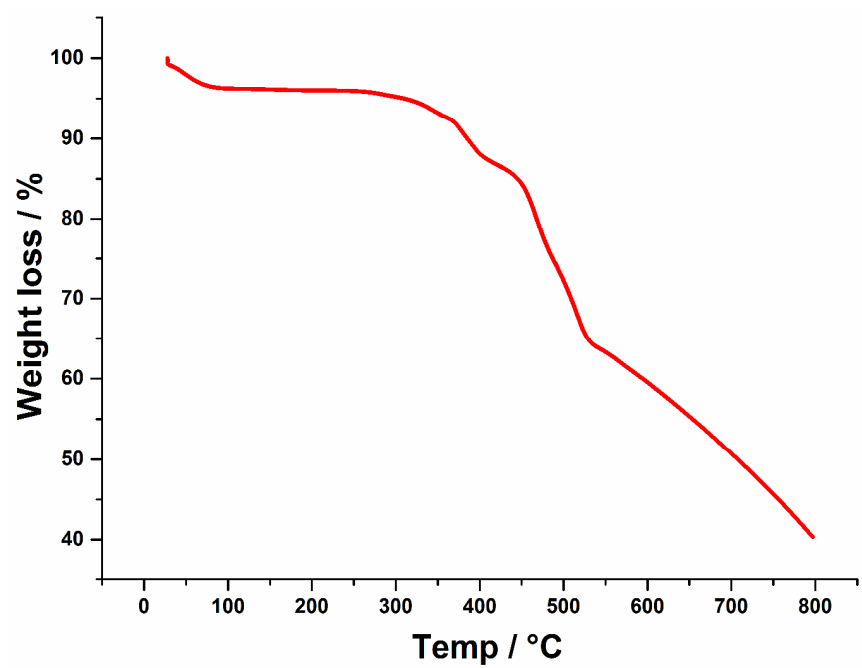


Figure S6. TG curve of complex 1.

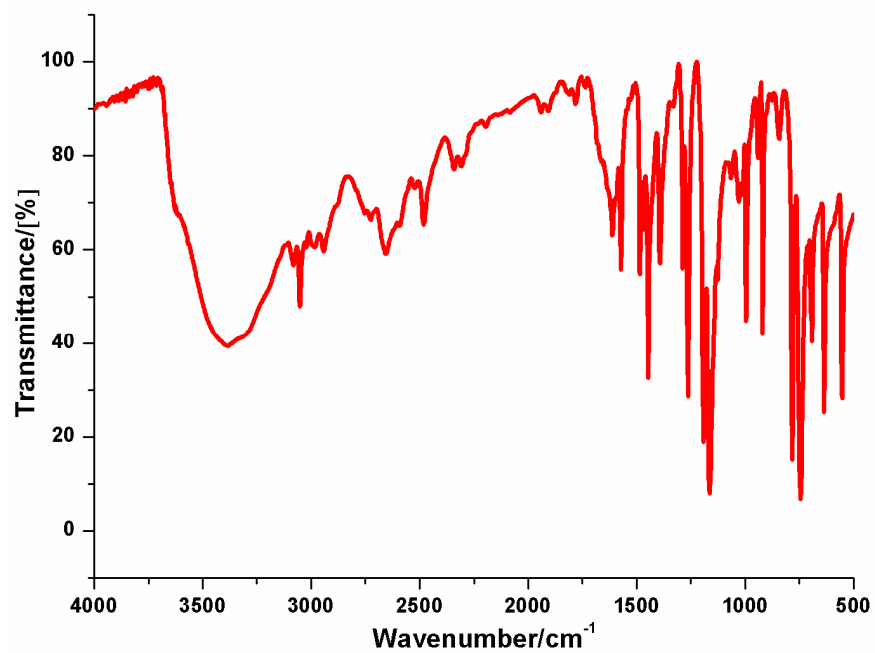


Figure S7. IR spectrum of complex 1.

Table S1. The selected bond lengths [Å] and angles [°] of complex **1**.

Mn(1)-N(3)	2.191(6)	Mn(1)-N(6)	2.237(6)
Mn(1)-N(1)	2.270(5)	Mn(1)-N(4)	2.303(5)
Mn(1)-Cl(2)	2.475(2)	Mn(1)-Cl(1)	2.6871(15)
Mn(2)-N(5)#1	2.242(6)	Mn(2)-N(5)	2.242(6)
Mn(2)-N(2)	2.248(6)	Mn(2)-N(2)#1	2.248(6)
Mn(2)-Cl(2)	2.5313(17)	Mn(2)-Cl(2)#1	2.5313(17)
Cl(1)-Mn(1)#2	2.6871(15)	Cl(1)-Mn(1)#3	2.6871(16)
Cl(1)-Mn(1)#4	2.6871(16)		
N(3)-Mn(1)-N(6)	107.5(2)	N(3)-Mn(1)-N(1)	165.5(2)
N(6)-Mn(1)-N(1)	84.8(2)	N(3)-Mn(1)-N(4)	85.6(2)
N(6)-Mn(1)-N(4)	166.3(2)	N(1)-Mn(1)-N(4)	81.7(2)
N(3)-Mn(1)-Cl(2)	92.59(16)	N(6)-Mn(1)-Cl(2)	93.63(16)
N(1)-Mn(1)-Cl(2)	94.21(15)	N(4)-Mn(1)-Cl(2)	89.76(16)
N(3)-Mn(1)-Cl(1)	88.53(16)	N(6)-Mn(1)-Cl(1)	90.84(15)
N(1)-Mn(1)-Cl(1)	83.61(15)	N(4)-Mn(1)-Cl(1)	85.30(15)
Cl(2)-Mn(1)-Cl(1)	174.83(5)	N(5)#1-Mn(2)-N(5)	94.5(3)
N(5)#1-Mn(2)-N(2)	175.3(2)	N(5)-Mn(2)-N(2)	89.8(2)
N(5)#1-Mn(2)-N(2)#1	89.8(2)	N(5)-Mn(2)-N(2)#1	175.3(2)
N(2)-Mn(2)-N(2)#1	86.0(3)	N(5)#1-Mn(2)-Cl(2)	91.15(19)
N(5)-Mn(2)-Cl(2)	86.66(19)	N(2)-Mn(2)-Cl(2)	91.03(17)
N(2)#1-Mn(2)-Cl(2)	91.32(17)	N(5)#1-Mn(2)-Cl(2)#1	86.66(19)
N(5)-Mn(2)-Cl(2)#1	91.15(19)	N(2)-Mn(2)-Cl(2)#1	91.32(17)
N(2)#1-Mn(2)-Cl(2)#1	91.03(17)	Cl(2)-Mn(2)-Cl(2)#1	176.78(10)
Symmetry transformations used to generate equivalent atoms:			
#1: x, -y+1/2, -z+1/4; #2: -y, x, -z; #3: -x, -y, z; #4: y, -x, -z.			