Supporting Information

Two-Dimensional Homochiral Manganese(II)-Azido Frameworks Incorporating an Achiral Ligand: Partial Spontaneous Resolution and Weak Ferromagnetism

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Experimental Details

Synthesis. The diazine ligand, 2-pyridylmethylketazine (PMK), were prepared according to the literature methods.[1]

CAUTION! Although not encountered in our experiments, azido and perchlorate compounds of metal ions are potentially explosive. Only a small amount of the materials should be prepared, and it should be handled with care.

A mixture of manganese(II) perchlorate hexahydrate (1 mmol) and sodium azide (2 mmol) in methanol (15 mL) was added with continuous stirring to PMK (0.5 mmol) in the same solvent (10 mL). The solution was stirred for 10 min and then allowed to evaporate slowly at room temperature, two kinds of yellow crystals with different shapes, prism (**1**) and hexagonal plate (**2**), appeared within two days, which were separated manually. Yields, *ca*. 34% and 20% for **1** and **2**, respectively.

Anal. Calcd for $C_{14}H_{14}Mn_2N_{16}$ (**1**): C, 32.57; H, 2.73; N, 43.41. Found: C, 32.53; H, 2.81; N, 43.56 %. Main IR bands: $\nu_{as}(N_3)$, 2102s, 2070sh, 2055vs; $\nu_s(N_3)$, 1325m; ν(C=N), 1594m.

Anal. Calcd for $C_{15}H_{18}Mn_2N_{16}O$ (**2**): C, 32.86; H, 3.31; N, 40.87. Found: C, 33.06; H, 3.55; N, 41.80 %. Main IR bands: $\nu_{as}(N_3)$, 2116s, 2086sh, 2069vs; $\nu_s(N_3)$, 1327m; ν(C=N), 1593m.

Crystallographic Studies. Diffraction intensity data for single crystals of **1** and **2** were collected at room temperature on a Nonius Kappa CCD diffractometer equipped with graphite-monochromated Mo *K*α radiation (λ = 0.71073 Å). Empirical absorption corrections were applied using the Sortav program.[2] The structure was solved by the direct method and refined by the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. [3] Hydrogen atoms were located geometrically and refined isotropically. See the CIF file for details.

Physical measurements. Elemental analyses (C, H, N) were performed on an Elementar Varia EL analyzer. IR spectra were recorded on a Nicolet Magna-IR 750 spectrometer equipped with a Nic-Plan Microscope. Magnetic measurements were performed on a Oxford MagLab 2000 magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms. Figure S1 gives the χ_M-T and $\chi_M T$-T plots at 5000 G.

Supplementary Magnetic Studies

The field dependence of magnetization was measured at 5.0 K as shown in Figure S2. At the highest field measured (50 kG), the magnetization values are 0.25 and 0.21 Nβ for **1** and **2**, respectively. These values are far below the saturation value expected for an S = 5/2 system (5 Nβ), consistent with weak ferromagnetism due to spin canting. The net magnetizations are very weak, indicating very small canting angles. The Cycling the applied field between +10 and -10 kG at 5 K generates a hysteresis loop for **1**, the central portion of which is shown in Figure S3, with a remnant magnetization of 1.76×10^{-3} Nβ and a coercive field of 140 G. No hysteresis was observed for compound **2**. To further confirm the weak ferromagnetic behaviors of the two compounds, the zero-field-cooled (ZFC) magnetization is measured upon warming at an applied field of 200 G. The results are plotted as *M vs*. *T* curves in Figure S4, in which the FC curves are also presented for comparison. These plots clearly indicate weak ferromagnetic transitions for both compounds. The two compounds exhibit not only different ordering temperatures, but also distinct FC and ZFC behaviors. Further investigations are needed to fully characterize the magnetic transitions.

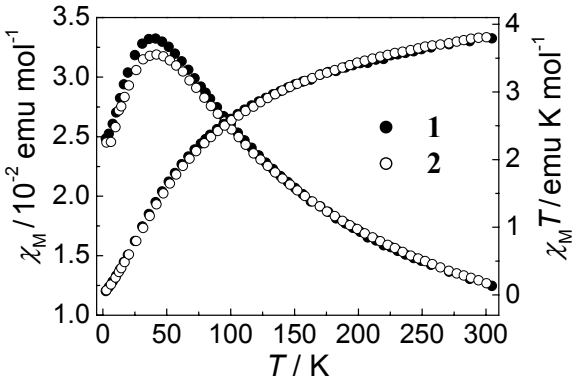

Figure S1. χ_M-T and χ_MT-T plots at 5000 G

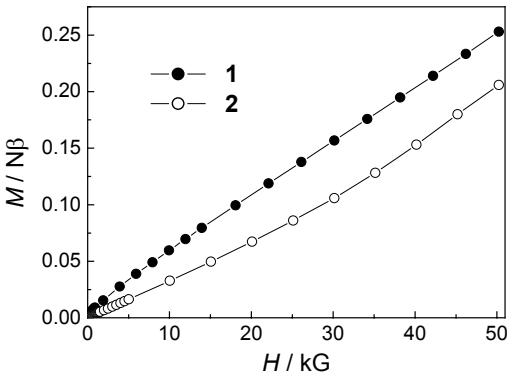

Figure S2. The field dependence of magnetization for **1** and **2** at 5.0 K

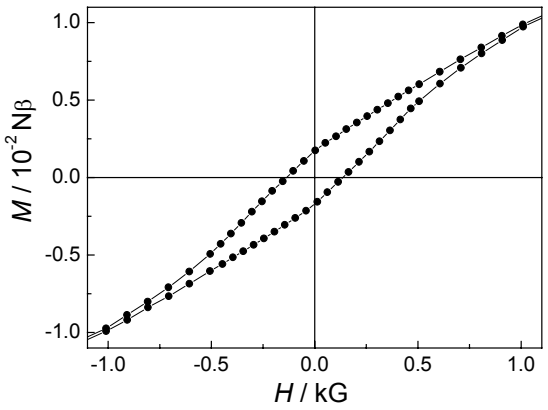

Figure S3. The hysteresis loop for **1** at 5.0 K

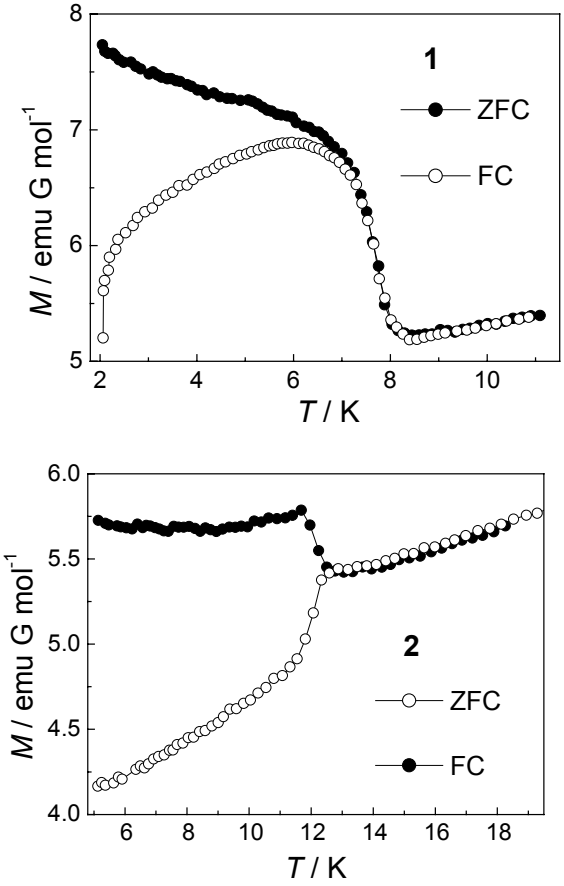

Figure S3. ZFC and FC magnetization at 200 G.

(1) Guo, D.; He, C.; Duan, C.-Y.; Qian, C.-Q.; Meng, Q.-J. *New J. Chem.* **2002**, *26*, 796.
(2) (a) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33. (b) Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421.
(3) (a) Sheldrick, G. M. SHELXTL Version 5.1. Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, **1998**. (b) Sheldrick, G. M. SHELXL-97, PC Version. University of Göttingen, Germany, **1997**.