ELECTRONIC SUPPLEMENTARY DATA

For

A 3D Homometallic Carboxylate Ferrimagnet Constructed from a Manganese(II) Succinate Carboxylate Layer Motif Pillared by Isonicotinate Spacers

Ming-Hua Zeng,*,[†] Mei-Chun Wu,[†] Hong Liang,*,[†] Yan-Ling Zhou,[†]
Xiao-Ming Chen,[‡] Seik-Weng Ng§

[†]Department of Chemistry and Chemical Engineering, GuangXi Normal University, Guilin 541004, P. R. China Fax: Int. code +86 773 5812-383. E-mail: zmh@mailbox.gxnu.edu.cn.

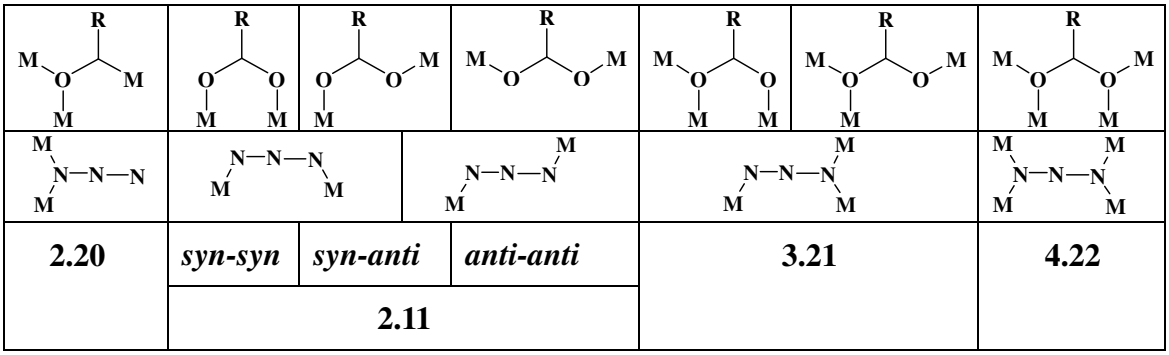
Experimental Section

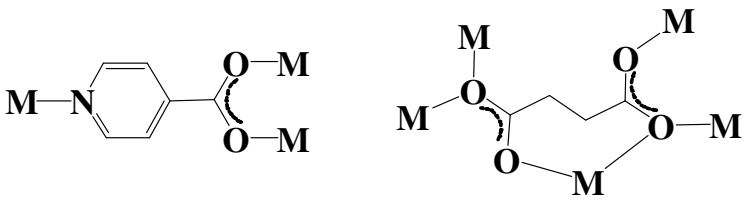
Succinic acid (0.118 g, 1 mmol) in an aqueous solution (6 mL) of NaOH (0.080 g, 2 mmol) was mixed with isonicotinic acid (0.123 g, 1 mmol) in water (2 mL), which was then added to an aqueous solution (2 mL) of $MnCl_2{\cdot}4H_2O$ (0.197 g, 1 mmol). The mixture was placed in a 23 mL Teflon-lined autoclave and heated at 130°C for 96 hrs. The autoclave was cooled over a period of 12 hrs at a rate of 5 °C h^{-1}, and **1** as pale-yellow crystals were collected by filtration, washed with water, and dried in air, the final pH of the solution is *ca*. 5.5. The phase pure **1** was obtained by manual separation (yield: 102 mg, *ca*. 30% based on Mn). Anal. Calcd. (%) for $C_{20}H_{16}Mn_3N_2O_{12}$: C, 37.47; H, 2.52; N, 4.37; found C, 37.40; H, 2.56; N, 4.33%. IR data: 1597*vs*, 1551*s*, 1387*vs*, 1288*m*, 1206*m*, 869*w*, 770*m*, 697*m*, 515*w*, 434*w*.

The single crystal diffraction data were measured with a Bruker Smart Apex CCD system. The structure was solved by direct methods and refined using full-matrix least-squares technique using SHELXTL. All non-hydrogen atoms were refined with anisotropic displacement parameters, while the hydrogen atoms of the ligands were refined as riding atoms. Crystalorgraphic data for **1**: $C_{20}H_{16}Mn_3N_2O_{12}$, M_r = 641.17, triclinic, space group *P*-1, a = 7.649(3), b = 8.916(3), c = 9.472(3) Å, V = 554.0(3) $Å^3$, α = 68.858(5)º, β = 85.627(5)º, γ = 67.227(5)º, Z = 1, T = 293(2) K, D_c = 1.922 Mg m^{-3}, (Mo-Kα) = 1.74 mm^{-1}, F(000) = 321. Final R_1 and wR_2 (all data) = 0.0241 and 0.0563, and S = 1.10.

Magnetic measurements: magnetic susceptibility measurements of **1** were performed on a polycrystalline sample on a Quantum Design MPMS-XL7 SQUID. Data were corrected for the diamagnetic contribution calculated from Pascal constants and the diamagnetism of the sample and sample holder were taken into account.

Scheme S1. The Bridging Mode for μ-$RCOO^-$ and μ-N_3^-





Scheme S2. Coordination modes of suc and ina ligands in **1**.

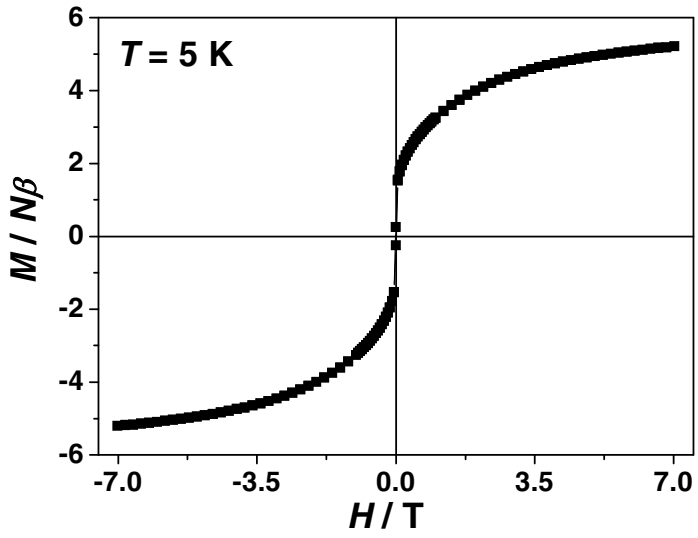


Figure S1a. Magnetization plot at 5 K for compound **1** in the ±7 T range (per three Mn^{II} ions).

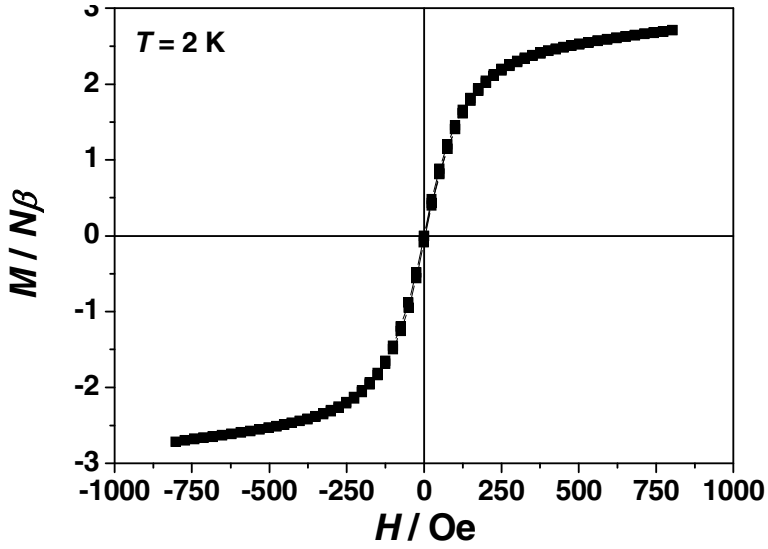


Figure S1b. Magnetization plot at 2 K for compound **1** in the ±800 G range (per three Mn^{II} ions).

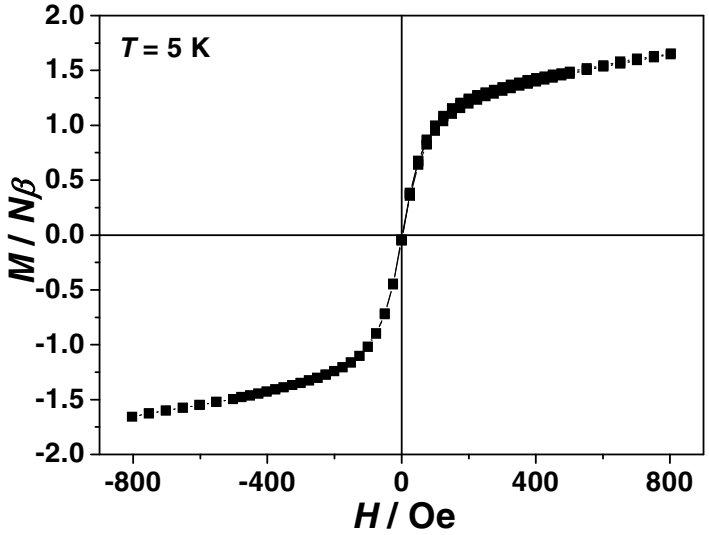


Figure S1c. Magnetization plot at 5 K for compound **1** in the ±800 G range (per three Mn^{II} ions).

Least-square fitting of the magnetic data for **1:**

Given the spin value a convenient expression may be deduced from a classical spin model, using the spin Hamiltonian where J_1 and J_2 stand for the exchange interactions and where the S_n are classical spin vectors. This approximation is fully justifiable when studying manganese(II) chains that exhibit large spins (S = 5/2). The wave-vector-dependent susceptibility is

$$H = -J_1 \sum (S_{3i} S_{3i+1} + S_{3i+1} S_{3i+2}) - J_2 \sum S_{3i-1} S_{3i}$$

For the alternating chain, the pair correlation function must be written as

$\langle SnSn{+}p\rangle = u_1u_1u_2u_1...$

with

$$u_1 = \coth(\frac{J_1}{kT}) - \frac{kT}{J_1} \qquad u_2 = \coth(\frac{J_2}{kT}) - \frac{kT}{J_2} \qquad C = Ng^2\mu_B^2/(3kT)$$

Taking into account the *p* parity, the above expression reduces To

$$S(q) = 1/kT\ \{3(1 - u_1^4u_2^2) + 2(2u_1 + u_2 - u_1^3u_2(u_1 + 2u_2))\cos(qa) + 2(u_1^2 + 2u_1u_2 - 2u_1^3u_2 - u_1^2u_2^2)\cos(2qa)\ \}\{1 - 2u_1^2u_2\cos(3qa) + u_1^4u_2^2\}^{-1}$$

Then we obtain the expression of the bulk susceptibility, corresponding to the $q = 0$ limit, for the alternating chain $J_1J_1J_2\ \cdots$ as which reduces to the uniform chain solved by Fisher[11] for $u_1 = u_2$ (C takes the usual meaning $C = Ng^2\mu_B^2/(3kT)$).

$$\chi = \frac{C}{(1-u_1^2u_2)^2}\{3(1-u_1^4u_2^2) + 4u_1(1-u_1^2u_2^2) + 2u_2(1+u_1)^2(1-u_1)^2 + 2u_1^2(1-u_2^2)\}$$

$$J_i \rightarrow J_iS(S+1) \qquad g \rightarrow g(S(S+1))^{1/2} \qquad \text{(Equation S1)}$$

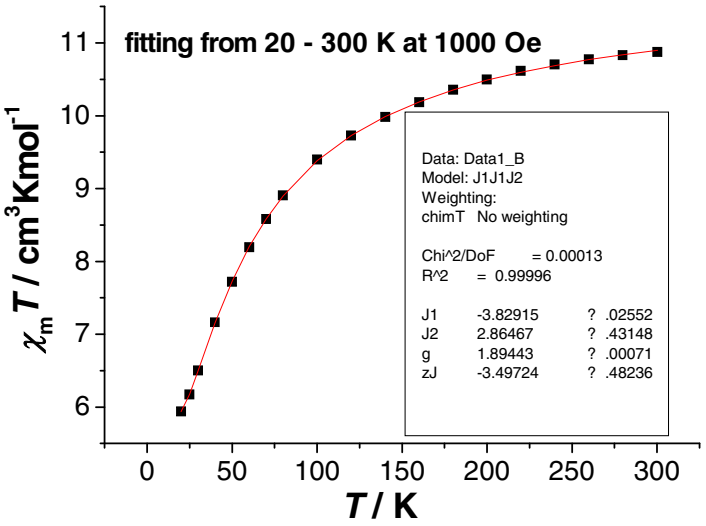


Figure S2. Plot of $\chi_M T$ *vs*. *T*. Solid line represents the best fit with the parameters given in the text.

(11) Fisher, M, E. *Am. J. Phys*. **1974**, *32*, 241.

(12) Abu-Youssef, M. A. M.; Drillon, M.; Escuer, A.; Goher, M. A. S.; Mautner, F. A.; Vicente, R. *Inorg. Chem.* **2000**, *39*, 5022.

Adjusting the so calculated values of $\chi_M(T)$ to the measured susceptibility $\chi_M^{exp}(T)$ data (20 ~ 300 K), and obtain the parameters: g = 1.89, J_1 = - 3.83 cm^{-1}, J_2 = 2.86 cm^{-1}, and zJ = - 3.49 cm^{-1} (Where, J_1, J_2 is the intra-trimer exchange interaction, J is the inter-chains exchange interaction and z is the number of nearest neighbors of the chains.). and R is residual factor defaulted as $R = \Sigma(\chi_{obs}T - \chi_{cal}T)^2/\Sigma(\chi_{obs}T)^2$.