

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,[‡] and Seik-Weng Ng[§]

Department of Chemistry and Chemical Engineering, GuangXi Normal University, Guilin 541004, People's Republic of China, MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, People's Republic of China, and Department of Chemistry, University of Malaya, Kuala Lumpur 50603, Malaysia

Received April 30, 2007

A manganese succinate having a layer structure in which the layers are pillared by the isonicotinate spacers in a 3D architecture exhibits long-range ferrimagnetic order below 5.0 K, with the ferrimagnetism arising, for topological reasons, from the nature of the carboxylate binding modes. The compound is the first structurally authenticated example of a 3D ferrimagnet, featuring a homometallic topological ferrimagnetic sheet among metal carboxylates.

Conventional ferrimagnetic systems of metal complexes (i.e., heterospin systems contain two different magnetic ions with nearest-neighbor antiferromagnetic exchange coupling) are well represented by numerous compounds whose metal atoms are bridged through, for example, cyanide or oxalate groups.¹ For such bridged compounds, long-range ferrimagnetic order arises from the noncompensation of the differently individual spin moments. On the other hand, only a few homospin homometallic systems are known that exhibit long-range ferrimagnetic order,^{2,3} with the reason for such scarcity being linked to the necessity for the noncompensation moments, which is difficult to achieve in practice because only one kind of spin is involved.^{2b} The reported systems displaying such order, as represented by azide-bridged complexes, homometallic molecular ferrimagnets based on

azide, or carboxylate and/or hydroxide bridges, are, however, restricted to linear spin topology only,^{2,3} as noted from literature accumulated over the last several decades. It is only recently that the first example of a sheetlike homometallic ferrimagnet involving a manganese azide was reported;^{2a} the report confirms the ability of heteroligand systems to reach ferrimagnetic response in homometallic systems.

Chief among the requirements is a predetermined molecular topology, such as a specific alternation of ferromagnetic (F) and antiferromagnetic (AF) interactions; the term “topological ferrimagnetism” is now used to describe this phenomenon that these interaction topologies, where F and AF interactions coexist, allow the appearance of magnetic behavior in a homopolynuclear system similar to the ferrimagnetic behavior observed in heteropolynuclear systems.² On the other hand, carboxylate ligand chemistry has always provided a plethora of examples, from discrete molecules to complicated 3D networked polymers.⁴ More importantly, because the carboxyl entity in a carboxylic acid can, and often does, engage in multiple bridging modes (Scheme S1 in the Supporting Information) [such as the ubiquitous syn–syn, anti–anti, and syn–anti, the less-common 1,1,3- μ_3 -, the rare 1,1- μ_2 -, and the 1,1,3,3- μ_4 -carboxylate modes], this entity is capable of promoting F or AF interactions.⁴ Molecular magnetism of metal carboxylates, such as AF, spin canting, spin glasses, and metamagnetic properties in the low temperature, has now been observed for many transition-metal complexes.^{4–6} Only a few examples of them exhibit a ferrimagnetic phase transition that features a linear arrangement

* To whom correspondence should be addressed. E-mail: zmh@mailbox.gxnu.edu.cn (M.-H.Z.), hliang@mailbox.gxnu.edu.cn (H.L.). Tel: 86 773 5812-773. Fax: 86 773 5812-383.

[†] GuangXi Normal University.

[‡] Sun Yat-Sen University.

[§] University of Malaya.

- (1) Mathoniere, C.; Sutter, J. P.; Yakhmi, J. V. In *Magnetism: Molecules to Materials II*; Miller, J. S., Drillon, M., Eds.; Wiley-VCH: Weinheim, Germany, 2003; pp 1–44.
- (2) (a) Escuer, A.; Mautner, F. A.; Goher, M. A. S.; Abu-Youssef, M. A. M.; Vicente, R. *Chem. Commun.* **2005**, 605. (b) Abu-Youssef, M. A. M.; Escuer, A.; Goher, M. A. S.; Mounter, F. A.; Reib, G. J.; Vicente, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 1624. (c) Gao, E.-Q.; Yue, Y.-F.; Bai, S.-Q.; He, Z.; Yan, C.-H. *J. Am. Chem. Soc.* **2004**, *126*, 1419. (d) Chen, H.-J.; Mao, Z.-W.; Gao, S.; Chen, X.-M. *Chem. Commun.* **2001**, 2320. (e) Ghosh, A. K.; Ghoshal, D.; Zangrando, E.; Ribas, J.; Chaudhuri, N. R. *Inorg. Chem.* **2005**, *44*, 1786. (f) Cano, J.; Journaux, Y.; Goher, M. A. S.; Abu-Youssef, M. A. M.; Mautner, F. A.; Reib, G. J.; Escuer, A.; Vicente, R. *New J. Chem.* **2005**, *29*, 306.

- (3) (a) Wang, R.-H.; Gao, E.-Q.; Hong, M.-C.; Gao, S.; Luo, J. H.; Lin, Z. Z.; Han, L.; Cao, R. *Inorg. Chem.* **2003**, *42*, 5486. (b) Li, J. T.; Tao, J.; Huang, R. B.; Zheng, L. S.; Yuen, T.; Lin, C. L.; Varughese, P.; Li, J. *Inorg. Chem.* **2005**, *44*, 4448. (c) Konar, S.; Mukherjee, P. S.; Zangrando, E.; Lloret, F.; Chaudhuri, N. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 1651. (d) Humphrey, S. M.; Wood, P. T. *J. Am. Chem. Soc.* **2004**, *126*, 13236. (e) Guillou, N.; Pastre, S.; Livage, C.; Férey, G. *Chem. Commun.* **2002**, 2358.
- (4) (a) Rao, C. N. R.; Natarajan, S.; Vaidyanathan, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 1466. (b) Janiak, C. *J. Chem. Soc., Dalton Trans.* **2003**, 2781.

COMMUNICATION

of homospins, and these compounds are systems that have the metal centers linked through mixed hydroxyl/carboxylate bridges.³ As is well-documented in other cases, an example of a layer type of carboxylate-based “topological ferrimagnetism” has not been structurally verified yet. The main difficulty for synthesizing such a compound involves uncompensated individual homospin moments through the properly arrayed carboxylate bridges.^{6c} This Communication presents an unprecedented example of a 3D pillar-layered metal carboxylate (Figure 1), [Mn₃(suc)₂(ina)₂]_n (suc = succinate and ina = isonicotinate), that possesses the crucial manganese(II) 1,1,3- μ_3 - and 1,3- μ_2 -carboxylate layer motif. It is the first 3D ferrimagnet with a 2D homometallic topological ferrimagnetic molecular sheet among metal carboxylates.

X-ray diffraction analysis indicates that there are two crystallographically independent Mn^{II} centers in the linear trinuclear subunit (Figure 1a). Atom Mn1 is located at an inversion site and is coordinated by six trans-related carboxylate O atoms, four from different suc dianions [Mn1–O = 2.152(1)–2.192(1) Å] and two from ina anions [Mn1–O = 2.124(1) Å] in an octahedral geometry. The other two Mn^{II} are six-coordinate in an octahedral geometry because each is coordinated by a pyridyl N atom, one carboxylate O atom from the ina ligand [Mn2–O = 2.141(2) Å; Mn2–N1 = 2.327(2) Å], and four carboxylate O atoms from three different suc ligands [Mn2–O = 2.151(1)–2.258(1) Å]. Each suc is coordinated to five Mn atoms through two similar 1,1,3- μ_3 -bridging carboxylate groups, whereas each ina binds in an exo-tridentate bridging mode through the pyridyl N atom and 1,3- μ_2 -carboxylate group (Scheme S2 in the Supporting Information). As such, the central Mn atom is linked to the other two Mn atoms by one syn–syn μ_2 -carboxylate bridge, one μ -O atom in the μ_3 -carboxylate group from two different suc ligands, and one syn–syn μ_2 -carboxylate bridge of ina, to give rise to a trinuclear Mn subunit with an Mn–O–Mn angle of 113.5(1)°. The Mn···Mn distance of 3.707 Å (atom to atom) is significantly longer than those in carboxylate-bridged trinuclear Mn^{II} complexes.^{3a,b} The two other μ -O atoms in the μ_3 -carboxylate bridge of suc equivalents link the trinuclear Mn^{II} subunits into a linear chain, and all of the metal atoms are nearly coplanar. The shortest intercluster Mn···Mn distance within the chain is 3.530 Å [Mn–O–Mn = 103.6(1)°], and the intertrimer double μ -O bridge has Mn2–O–Mn2b angles within a range for which F coupling between two Mn centers has been observed.^{3a,b} The Mn1 and Mn2 atoms are also linked to the Mn1 and Mn2 equivalents in an adjacent chain through two syn–anti and two syn–syn carboxylate bridges (6.161 and 4.292 Å, respectively) that is approximately orthogonal to the above chain. These interactions lead to a rigid layer, which can be roughly described as a layer of

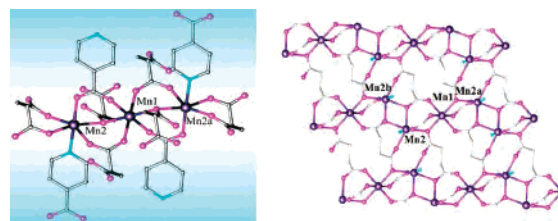


Figure 1. Plots of the Mn^{II} environments (a, left) and a 2D sheet (b, right) showing the carboxylate bridges within and between the Mn(2)–Mn(1)–Mn(2a) trimers in **1**. Color code: navy, Mn^{II}; pink, O; blue, N; light gray, C. The H atoms are omitted for clarity.

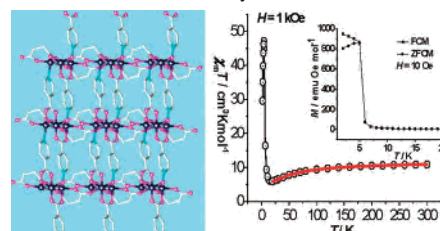


Figure 2. Plot of a 3D pillar-layered structure of **1** (a, left). $\chi_M T$ vs T for **1**. The red solid line represents the best fit given in the text. Inset: field-cooled and zero-field-cooled magnetization curves (b, left).

alternate connection of the chains of an edge-sharing trimer Mn octahedron linked by carboxylate bridges running along the a axis (Figure 1b). The structure represents a rare example of an “inorganic” metal–oxygen layer interconnected by dicarboxylate ligands without the presence of any hydroxyl groups.^{6c} Such layers are further extensively pillared by μ_3 -ina ligands into a 3D metal–organic framework, with the layers stacking in an AA packing mode with the interlayer distance of ca. 9.23 Å (Figure 2a).

The magnetic data were measured by tightly putting the crushed polycrystalline samples together to prevent torquing of the crystallites of **1**. The magnetic behavior of **1** takes the form of a $\chi_M T$ vs T plot (per three Mn^{II} ions; Figure 2b) in the 2–300 K temperature range at 1 kG. The magnetic susceptibility above 30 K obeys the Curie–Weiss law with a Weiss constant, $\theta = -26.14$ K, and a Curie constant, $C = 11.85$ cm³ mol⁻¹ K. The $\chi_M T$ value of each Mn₃ unit (10.88 cm³ mol⁻¹ K; 8.89 μ_B) at 300 K is somewhat lower than that (13.1 cm³ mol⁻¹ K; 10.25 μ_B) expected for three magnetically isolated high-spin Mn atoms, which indicates the presence of a dominant AF interaction.^{3a} When the temperature is decreased, the $\chi_M T$ values only slightly decrease to a minimum (5.94 cm³ mol⁻¹ K) at 20 K. Below 20 K, $\chi_M T$ rapidly increases and reaches a high maximum value (47.14 cm³ mol⁻¹ K) at around 4.5 K before eventually falling to 29.60 cm³ K mol⁻¹ at 2.0 K. The gradual decrease of $\chi_M T$ below 4.5 K is best ascribed to a saturation effect. This curve is characteristic of ferrimagnetic behavior. The inset of Figure 2b shows the field-cooled and zero-field-cooled magnetization and indicates the occurrence of the phase transition near 5.0 K. The reduced molar magnetization ($M/N\beta$ value per three Mn^{II} ions) at 2 K tends to 5.34 $N\beta$, but the curve does not follow the Brillouin law (Figure 3a, inset). Indeed, there is a rapid and abrupt increase of $M/N\beta$ at low fields (Figure S1 in the Supporting Information). This is the signature of long-range order commented on above when dealing with the field-cooled and zero-field-cooled magnetization curves at low temperature. Hysteresis loops

(5) Wang, X.-Y.; Wei, H.-Y.; Wang, Z.-M.; Chen, Z.-D.; Gao, S. *Inorg. Chem.* **2005**, *44*, 572.

(6) (a) Zeng, M.-H.; Yao, M.-X.; Liang, H.; Zhang, W.-X.; Chen, X.-M. *Angew. Chem., Int. Ed.* **2007**, *46*, 1832. (b) Zeng, M.-H.; Zhang, W.-X.; Sun, X.-Z.; Chen, X.-M. *Angew. Chem., Int. Ed.* **2005**, *44*, 3079. (c) Zeng, M.-H.; Wang, B.; Wang, X.-Y.; Zhang, W.-X.; Chen, X.-M.; Gao, S. *Inorg. Chem.* **2006**, *45*, 7069. (d) Zeng, M.-H.; Feng, X.-L.; Zhang, W.-X.; Chen, X.-M. *Dalton Trans.* **2006**, 5294.

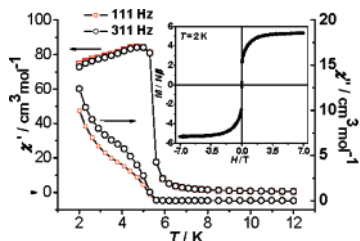
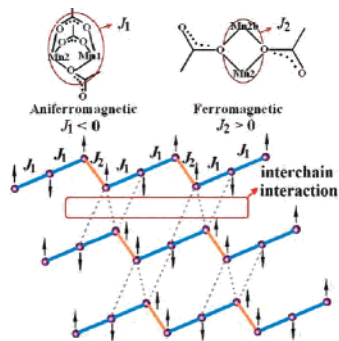


Figure 3. Real χ' and imaginary χ'' parts vs T at an ac field of 6 G for **1**. Inset: magnetization curve for **1** at 2 K.

Scheme 1. Spin Topology of the Mn^{II} Sheet in the Ground State Overlaid onto the Layered Structure of **1**



indicate that there is no noticeable hysteresis (a typical phenomenon in these soft magnets). An alternating current (ac) susceptibility measurement (Figure 3a) clearly corroborates the existence of long-range ferrimagnetic order below 5.0 K. The presence of an out-of-phase (χ'') signal is the typical signature. This signal is frequency-independent, indicating that the order is 3D, as was expected from the structure.⁷

This 3D ordering may be explained by the existence of the intralayer magnetic interactions of the adjacent chains for the manganese(II) carboxylate arrangement, that pillared by the ina units to give the 3D net. The ina bridges do not likely have any importance in terms of the long-range order. However, intralayer carboxylate bridges are very important. As shown in Scheme 1, according to the chain topology, there are two sets of magnetic exchange pathways within the chain: one consists of two syn–syn carboxylate bridges and a μ_2 -O bridge from the μ_3 -carboxylate group (J_1); the other mainly consists of two μ_2 -O bridges from two μ_3 -carboxylate groups (J_2 ; Scheme 1). To achieve noncompensation in spin moments within such a chain, the interaction through the former set of bridges must be AF and that through the latter set must be F. The interactions alternate according to an AF–AF–F repeating sequence to yield the spin topology that corresponds to a $(5, 5/2)$ ferrimagnetic chain with alternating interactions $J_1J_1J_2$. Individual ferrimagnetic chains interact with adjacent chains in dominant AF fashion from the contribution of the compensation through the multiple syn–anti (long) and syn–syn (short) carboxylate bridges. The 2D topological ferrimagnetic lattice formed by manganese carboxylate sheets elicits a long-order ferrimagnetic response even though it is a homometallic compound of **1**. On the other hand, the magnetic interaction through the ina linker is weak (usually an AF interaction); in the case of Mn^{II}, all of the d orbitals are singly occupied, and thus interaction through this linker cannot be ignored and still strongly influenced the bulk magnetic behavior of **1**.^{2d,7}

The magnitude of the coupling constants in the 3D networks of **1** cannot be calculated by conventional methods.^{7,8} To evaluate the interactions, with the molecular field approximation, a least-squares fit of the observed magnetic data based on the theoretical expression of 1D Heisenberg ferrimagnetic chains with alternating interactions $J_1J_1J_2$ (AF–AF–F), proposed by Escuer et al., was made (eq S1 and Figure S2 in the Supporting Information).⁹ The model provides a proper fit of $\chi_M T$ variation over the temperature range 20–300 K, with a discrepancy that does not exceed experimental uncertainty. The closest agreement between theory and experiment comes from the use of the following parameter values: $g = 1.89$, $J_1 = -3.83 \text{ cm}^{-1}$, $J_2 = 2.86 \text{ cm}^{-1}$, and $zJ = -3.49 \text{ cm}^{-1}$ (where J_1 and J_2 are the intrachain exchange interactions, J is the interchain exchange interaction, and z is the number of nearest neighbors of the chains). The J_1 value is comparable to those previously reported for trimanganese(II) complexes with similar bridging chains,³ and the J_2 value confirms that the unprecedented double μ -O bridges from the μ_3 -carboxylate groups mediate a F interaction, which may be due to accidental orthogonality between magnetic orbitals around the metal ions. The exchange interactions obtained with this model lie in the same range as those previously reported for manganese(II) carboxylate complexes.^{3,5} Upon a cooling of the temperature, the moderately high J_{AF} coupling, including intra- and interchain couplings [through μ -O (Mn–O–Mn = 113.5(1) $^\circ$) and 1,3-carboxylate bridges], promotes the antiparallel spin configuration and a net reduction of the magnetic moment. At very low temperature, the ferrimagnetic alignment of the resulting spins [due to double μ -O interactions (Mn–O–Mn = 103.6(1) $^\circ$)] becomes efficient and finally the $S_T = 5/2$ spin state per Mn₃ unit is achieved, in good agreement with the saturation value of magnetization.

In conclusion, **1** shows a unique 2D topological ferrimagnetic lattice formed by manganese(II) carboxylate sheets pillared by ina spacers to perform a 3D ferrimagnet, even as a homometallic carboxylate. The ferrimagnetic behavior in compound **1** further highlights the potential for creating an even number of AF interactions followed by one or more F interactions, which can be achieved through the properly arrayed carboxylate bridges in a homometallic carboxylate.^{3,10}

Acknowledgment. This work was supported by the NSFC (Grant 20561001), GKN (Grant 0630006-5D), and GJY (Grant 2006-26) as well as IPGGE (Grant 2006106020703M34).

Supporting Information Available: X-ray crystallographic data in CIF format for **1** and other information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC700832W

- (7) (a) Zeng, Y.-F.; Liu, F.-C.; Zhao, J.-P.; Cai, S.; Bu, X.-H.; Ribas, J. *Chem. Commun.* **2006**, 2227. (b) Liu, F.-C.; Zeng, Y.-F.; Jiao, J.; Bu, X.-H.; Ribas, J.; Battern, S. R. *Inorg. Chem.* **2006**, *45*, 2776.
- (8) Hatfield, W. E. In *Magneto-Structural Correlations in Exchange Coupled Systems*; Willet, R. D., Gatteschi, D., Kahn, O., Eds.; Reidel: Dordrecht, The Netherlands, 1984; p 555.
- (9) Abu-Youssef, M. A. M.; Drillon, M.; Escuer, A.; Goher, M. A. S.; Mautner, F. A.; Vicente, R. *Inorg. Chem.* **2000**, *39*, 5022.
- (10) (a) Zeng, M.-H.; Gao, S.; Yu, X.-L.; Chen, X.-M. *New J. Chem.* **2003**, *27*, 1599. (b) Zeng, M.-H.; Gao, S.; Chen, X.-M. *Inorg. Chem. Commun.* **2004**, *7*, 864.