Communication

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

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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. 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, with the reason for such scarcity being linked to the necessity for the noncompensation of the differently individual spin moments. 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, 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; 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.

On the other hand, carboxylate ligand chemistry has always provided a plethora of examples, from discrete molecules to complicated 3D networked polymers. 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, anti, the less-common 1,1,3,3-íanti, the rare 1,1,3,3-íanti, and the 1,1,3,3-íanti-carboxylate modes], this entity is capable of promoting F or AF interactions. 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. Only a few examples of them exhibit a ferrimagnetic phase transition that features a linear arrangement...
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 ferrimag-
netism” has not been structurally verified yet. The main
difficulty for synthesizing such a compound involves un-
compensated individual homospin moments through the
properly arrayed carboxylate bridges.6c This Communication
presents an unprecedented example of a 3D pillared-
metal carboxylate (Figure 1), [Mn(suc)(ina)]6 (suc = succ-
cinate and ina = isonicotinate), that possesses the crucial
manganese(II) 1,1,3-2-carboxylate O atoms, four from different suc ligands [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
1,1,3-2-carboxylate groups, whereas each ina binds in an exo-tridentate bridging mode through the pyridyl N atom and 1,3-2-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 2-carboxylate bridge, one μ-O atom in the μ-1-carboxylate group from
two different suc ligands, and one syn–syn 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 that in carboxylate-bridged trinuclear MnII
complexes.3ab The other two μ-O atoms in the μ-1-carboxylate bridge of suc equivalents link the trinuclear MnII 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.3ab 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 MnII 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 I. Color code: navy, MnII; pink, O; blue, N; light gray,
C. The H atoms are omitted for clarity.

Figure 2. Plot of a 3D pillared-layered structure of I (a, left), χMT vs T for
I. 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-syn
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 I. The magnetic behavior of I takes the form of a χMT vs T plot (per three MnII 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, θ = −26.14 K, and a Curie constant, C =
11.85 cm3 mol−1 K. The χMT value of each MnII unit (10.88
cm3 mol−1 K; 8.89 μb) at 300 K is somewhat lower than that
(13.1 cm3 mol−1 K; 10.25 μb) 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 χMT values only slightly
decrease to a minimum (5.94 cm3 mol−1 K) at 20 K. Below 20
K, χMT 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 χMT 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/Nβ) value per three MnII ions at 2 K tends to 5.34 Nβ,
but the curve does not follow the Brillouin law (Figure 3a,
inset). Indeed, there is a rapid and abrupt increase of M/Nβ
at low fields (Figure S1 in the Supporting Information). This
is the signature of long-range order commented above
when dealing with the field-cooled and zero-field-cooled
magnetization curves at low temperature. Hysteresis loops

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The magnitude of the coupling constants in the 3D networks of 1 cannot be calculated by conventional methods.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 $J_1J_2$ (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: $g = 1.89$, $J_1 = -3.83$ cm$^{-1}$, $J_2 = 2.86$ cm$^{-1}$, and $zJ = -3.49$ 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 $\mu$-O bridges from the $\mu$-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 $\mu$-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 $\mu$-O interactions (Mn—O—Mn = 113.6(1)$^\circ$) and 1,3-carboxylate bridges], 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

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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.

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References


