

Mn₃(HCOO)₆: a 3D porous magnet of diamond framework with nodes of Mn-centered MnMn₄ tetrahedron and guest-modulated ordering temperature†

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Mn₃(HCOO)₆, a 3D highly stable and flexible porous diamondoid framework based on Mn-centered MnMn₄ tetrahedral nodes, exhibits a wide spectrum of guest inclusion behaviour and long-range magnetic ordering with guest-modulated critical temperature.

With more and more porous coordination frameworks of various potential applications being prepared,¹ chemists have been trying to add functionalities other than porosity to these materials^{2–4} to achieve multi-functional materials. A long sought academic goal is to create a porous magnet since magnetism and porosity are inimical to one another.⁵ While long-range magnetic ordering requires moment carriers of short separation through short bridges, porosity relies on the use of extended connecting ligands. Existing porous magnets include metal–organic radical complexes,³ pillared layered metal hydroxides,⁶ and Prussian blue analogues.⁷ The possibility of modulating magnetic properties of porous magnets upon guest exchange renders them attractive for applications as magnetic sensors and devices.^{3,4} Here, we report a novel 3D porous magnet [Mn₃(HCOO)₆] containing bridging formate, a short ligand with a small stereo effect beneficial for the formation of coordination magnetic frameworks. Being totally different from the known formates,⁸ the material possesses a diamondoid framework with porous channels, high stability and flexibility for the inclusion of many kinds of guests, and long-range magnetic ordering with critical temperature modulated by guests.

The parent compound [Mn₃(HCOO)₆](CH₃OH)(H₂O) (**1**) was prepared by the reaction of MnCl₂·4H₂O with formic acid and triethylamine in methanol. X-Ray analysis‡ revealed an unusual diamondoid framework where its nodes are Mn-centered MnMn₄ tetrahedra (Fig. 1). The tetrahedra has one Mn ion (Mn1) at the center, four (Mn2, Mn3, Mn4 and Mn2A) at the apices, and six

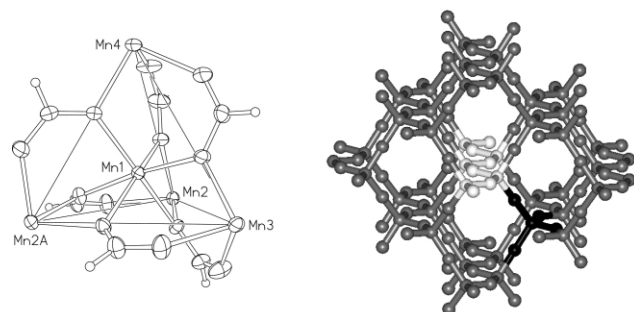


Fig. 1 Left: the Mn-centered MnMn₄ tetrahedron. Right: the topological presentation of the porous diamondoid framework formed by the tetrahedral units as nodes sharing apices, with one node highlighted in black and the central Mn1–Mn2 chain in white.

† Electronic supplementary information (ESI) available: element analysis, Fig. S1–S6 and Table S1. See <http://www.rsc.org/suppdata/cc/b3/b314221c/>

HCOO groups on the edges. The ligand has one O atom binding the central Mn and one apical Mn in *syn/anti* mode while other O atom is *syn*-binding one neighbouring apical Mn atom.⁹ By sharing their metal apices these tetrahedra form a diamondoid framework in which all metal atoms possess octahedral coordination geometry. This feature is quite striking because in most diamondoid coordination frameworks¹⁰ the metal atoms usually have tetrahedral coordination geometry. In the structure Mn1–Mn2 has two Mn–O–Mn and one M–O–C–O–M bridges while Mn1–Mn3 and Mn1–Mn4 have one Mn–O–Mn and two M–O–C–O–M bridges. From a magnetic point of view, the structure is best described as chains of edge-sharing Mn1 and Mn2 octahedra further connected by Mn3 and Mn4 octahedra *via* apex-sharing (Fig. 2, inset). The Mn1–Mn2 distances are alternately 3.292 and 3.323 Å and the Mn–O–Mn angles in pairs, 99.4° and 97.8°, and 96.4° and 97.5°. The Mn1–Mn3 connectivity is 3.625 Å and Mn1–Mn4 3.588 Å with the Mn–O–Mn angles of 113.1° (Mn3) and 110.4° (Mn4). The apical Mn–Mn distances are 5.429–5.825 Å.

The structure is an open-framework with channels (Fig. 1 and Fig. S1 in ESI†) running along the *b* direction. The channel is about 4 × 5 Å wide with the exclusion of the VDW radii of the surface atoms, and the void space is 32%. The solvent molecules lying in the channels are easy removed, as demonstrated by the thermogravimetric analysis (TGA, Fig. S2). Most guest molecules are removed below 100 °C, and the open framework is thermally stable up to ~260 °C. It therefore belongs to those porous coordination frameworks of high thermal stability.^{1,6,11} The desolvated form [Mn₃(HCOO)₆] (**2**) was prepared by heating **1** under vacuum at 110

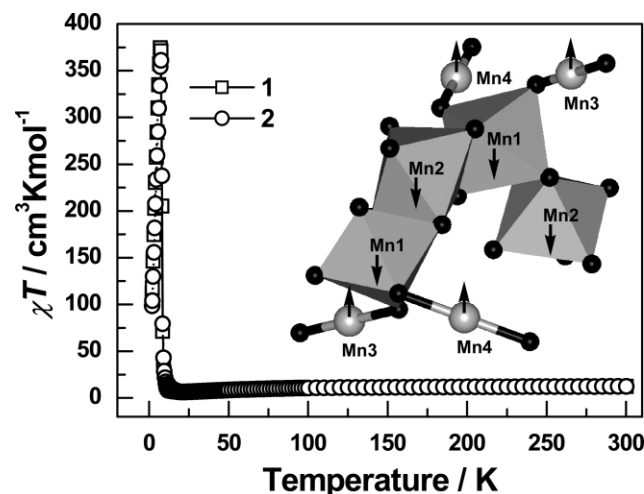


Fig. 2 The temperature dependence of the magnetic susceptibility of **1** and **2** in an applied field of 100 Oe. The data above 40 K fit the Curie–Weiss law with $C = 13.62$ and $13.48 \text{ cm}^3 \text{ K mol}^{-1}$, and $\theta = -31$ and -28 K for **1** and **2**, respectively. Inset, the chain of edge-sharing Mn1 and Mn2 octahedra with apex-sharing Mn3 and Mn4 octahedra, and the proposed magnetic structure.

°C, and the X-ray analysis‡ on a single crystal of **2** revealed the same framework with empty channels. The porosity is further justified by guest-inclusion experiments§ on **2**. Crystals of **2** can absorb more than 30 kinds of guests, both small and polar such as DMF and acetic acid, and large and non-polar such as benzene, naphthalene and tetrathiafulvalene, while still keeping their crystalline status with large cell volume changes¹¹ up to 9%.§ The channel can take up both hydrophilic and hydrophobic guests, in agreement with the fact that the lining consists of alternate arrays of C–H groups and oxygen atoms (Fig. S1). So far, the X-ray structures of five guest-inclusion compounds, acetic acid (**3**), DMF (**4**), furan (**5**), benzene (**6**) and iodine (**7**), have revealed the 1D molecular arrays of guests inside the channels (Fig. S3) with unchanged framework. TGA (Fig. S2) also confirmed the guest inclusion.

The observation of short metal–metal separations *via* single- and three-atom bridges in the porous framework appears promising for long range magnetic ordering. Indeed, **1–7** exhibit long-range magnetic ordering at low temperature and similar magnetic behavior (Fig. 2, 3, S4 and S5). For **1** and **2** (Fig. 2), the χT values first decrease when temperature goes down, and below 20 K they rise sharply to a maximum around 7 K, then decrease moderately again. The behavior is characteristic of ferrimagnets. The long-range ordering is further characterized by the ZFC/FC measurements at low field (Fig. 3) giving critical temperatures (T_c) of 8.1 K for **1** and 8.0 K for **2**. They are very soft magnets (Fig. S4). The magnetization rises sharply in low field range, and the saturation magnetizations are slightly larger than $5 N\beta$.

The magnetic behavior can be understood based on the structure and the Goodenough–Kanamori rule.¹² The octahedral Mn^{2+} has isotropic high spin $S = 5/2$. Considering the distances and angles between the Mn atoms in the different superexchange pathways, we can generalize that the Mn–O–Mn exchange between Mn1 and Mn2 would be fairly strong and ferromagnetic (Mn–O–Mn angles close to 98°), while those between Mn1 and Mn3 or Mn4 are weak and antiferromagnetic (Mn–O–Mn angles greater than 110°). Consequently, the proposed magnetic structure is ferromagnetic chains of –Mn1–Mn2– coupled antiferromagnetically to bridging Mn3 and Mn4 (Fig. 2, inset). Other exchange interactions are very weak due to the large distances. The saturated magnetization close to the value of $5 N\beta$ expected for the resultant moment of one Mn^{2+} per formula supports the proposed magnetic model.

The main effect of included guests on the magnetic property of the framework is the change of the critical temperature. T_c 's are 4.8, 7.2, 9.7, 8.6 and 7.1 K for **3**, **4**, **5**, **6** and **7** respectively, compared with 8.1 K for **1** and 8.0 K for **2** (Fig. 3). The structural parameters of these seven compounds show that the larger the key Mn1–O–Mn2 bond angles, the lower the T_c of the materials (Fig. S6). This structure–magnetism relationship is qualitatively consistent with the estimation from Kahn and Briat's approach, reviewed by Kalkeren *et al.*,¹³ and similar to an earlier case of the di-hydroxo-bridged Cu^{II} dimmers series.¹⁴ The guest inclusion does not change the framework structure much more than that in other reported

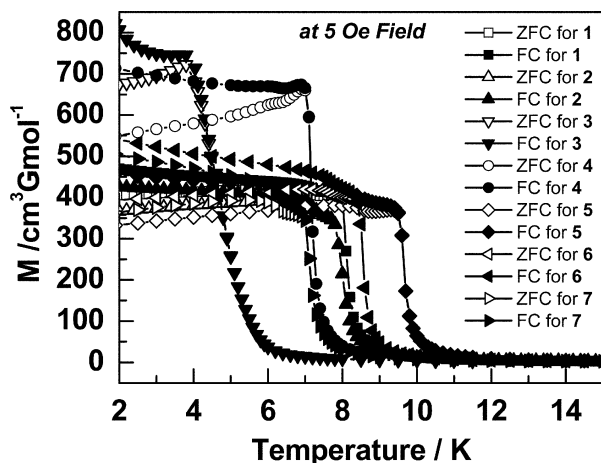


Fig. 3 ZFC/FC measurements for **1–7** in a 5 Oe field.

systems^{3,4} but modified the key structural parameters therefore the magnetic behaviour.

In conclusion, we have prepared a highly stable open framework that displays porosity and 3D long-range magnetic ordering. The material shows an unprecedented and flexible diamondoid framework based on Mn-centered $MnMn_4$ tetrahedral nodes and has a wide range of guest-inclusion ability. It demonstrates a new porous magnet with guest-modulated magnetic properties. Finally, it is worth pointing out that the wide spectrum of guest-inclusion behaviour of this magnetic framework indicates the possibility of combining functional guests such as radicals, photoactive or conductive units within the porous magnetic framework so that new magneto-magnetic, photo-magnetic or magneto-conductive materials are expected, and these researches are in progress.

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Notes and references

‡ Crystal data: for **1** at 180 K: $C_7H_{12}O_{14}Mn_3$, monoclinic, $P2_1/c$, $a = 11.650(1)$, $b = 10.128(1)$, $c = 18.614(2)$ Å, $\beta = 127.056(3)^\circ$, $U = 1752.6(3)$ Å³, $R1 = 0.0305$, $wR2 = 0.0836$. For **2** at 180 K: $C_6H_6O_{12}Mn_3$, monoclinic, $P2_1/c$, $a = 11.729(1)$, $b = 10.192(1)$, $c = 18.742(2)$ Å, $\beta = 127.178(3)^\circ$, $U = 1785.2(3)$ Å³, $R1 = 0.0302$, $wR2 = 0.0622$. For **3** at 90 K: $C_9H_{12}O_{14}Mn_3$, monoclinic, $P2_1/c$, $a = 11.688(2)$, $b = 10.244(2)$, $c = 18.753(4)$ Å, $\beta = 127.408(3)^\circ$, $U = 1783.6(6)$ Å³, $R1 = 0.0532$, $wR2 = 0.1475$. For **4** at 94 K: $C_9H_{13}NO_{13}Mn_3$, monoclinic, $P2_1/c$, $a = 11.705(2)$, $b = 10.095(1)$, $c = 18.556(3)$ Å, $\beta = 127.585(2)^\circ$, $U = 1737.5(4)$ Å³, $R1 = 0.0312$, $wR2 = 0.0624$. For **5** at 90 K: $C_{10}H_{10}O_{13}Mn_3$, monoclinic, $P2_1/c$, $a = 11.519(2)$, $b = 10.005(2)$, $c = 18.685(4)$ Å, $\beta = 126.821(3)^\circ$, $U = 1723.8(5)$ Å³, $R1 = 0.0370$, $wR2 = 0.0882$. For **6** at 82 K: $C_{12}H_{12}O_{12}Mn_3$, monoclinic, $P2_1/c$, $a = 11.655(2)$, $b = 10.162(1)$, $c = 19.042(3)$ Å, $\beta = 126.580(2)^\circ$, $U = 1811.0(4)$ Å³, $R1 = 0.0298$, $wR2 = 0.0620$. For **7** at 82 K: $C_6H_6O_{12}I_{1.74}Mn_3$, monoclinic, $P2_1/c$, $a = 11.834(2)$, $b = 10.196(1)$, $c = 18.848(3)$ Å, $\beta = 127.905(2)^\circ$, $U = 1794.4(4)$ Å³, $R1 = 0.0329$, $wR2 = 0.0884$. CCDC reference numbers 210639–210640 and 218686–218690.

§ Research on guest inclusion of this porous magnet is in progress and the detailed results will be reported elsewhere. Currently the minimum cell volume U of 1681.3 Å³ is observed for the acetonitrile inclusion compound and the maximum U of 1844.4 Å³ for the chlorobenzene inclusion compound. Thus the framework allows volume changes up to 9%.

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