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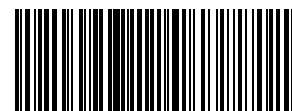**COMMUNICATION**
Srinivasan Natarajan *et al.*
A three-dimensional metal–organic framework with a distorted Kagome related layer showing canted antiferromagnetic behaviour

FEATURE ARTICLE
Anthony K. Burrell, Mark T. McCleskey and Q. X. Jia
Polymer assisted deposition

A three-dimensional metal–organic framework with a distorted Kagome related layer showing canted antiferromagnetic behaviour†

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Three-dimensional [Mn₃{C₆H₃(COO)₃}₂] comprising two-dimensional –Mn–O–Mn– distorted Kagome layers, formed by two geometrically different hexa-coordinated Mn²⁺ ions, show less frustration and spin canted long range ordering possibly due to antisymmetric exchange.

Metal–organic frameworks (MOFs) based on transition metal elements are an important family as they provide an opportunity to correlate their structure and magnetism, in addition to their adsorption and related properties arising out of the porous structure.[1] Recently, two-dimensional (2D) spin-half antiferromagnets have generated considerable interest due to the observation of superconductivity and spin chirality.[2] Among the 2D lattices,[2b] the Kagome lattice, possessing either 3- or 6-fold symmetry within the layers, occupies an important position for the observation of magnetic frustration. Most of the magnetic studies of Kagome structured materials are with jarosite, $KFe_3(SO_4)_2(OH)_6$, and its analogues.[3] Recently Rao and Nocera and co-workers independently studied various transition metal based jarosite related compounds with particular emphasis on the magnetic properties of Kagome structures.[4,5] Zaworotko and co-workers reported the first crystal engineered Kagome lattice whose lattice vertexes are occupied by paramagnetic dicopper(II) tetracarboxylate spin pairs.[6] The Cu^{2+} ions within the dimer are coupled antiferromagnetically, but the bridges between the dimers are too long to allow effective magnetic coupling. Recently Gao and co-workers prepared a Co^{2+} compound, $Co(N_3)_2(bpg)(DMF)_{4/3}$, with a Kagome lattice, which shows both frustration and long range ordering.[7] Kagome-like topologies, though few, have been observed in other MOFs and related systems as well.[8] In jarosite structures, the metal centers are connected through a single atom (O, F, OH *etc.*),[4,5] but there are no reports of similar layers in MOFs. Recently, we have reported the formation of a brucite related structure, $[Mn(OH)]_2[C_{12}H_8O-(COO)_2]$ where the metal centers are bridged by a single atom (O, OH).[9] Continuing a similar strategy and employing trimellitic acid (1,2,4-benzene tricarboxylic acid, BTC) along with Mn^{2+} ions, we have isolated a unique solid possessing a distorted Kagome layer in which the metal centers are connected by a single atom (O). The three-dimensional compound $[Mn_3\{C_6H_3(COO)_3\}_2]$, **I**, has distorted Kagome layers formed by two geometrically different Mn^{2+} ions, connected by the trimellitate anions. This is the first observation, to our knowledge, of the metal ions being connected by a single bridging atom to form a distorted Kagome layer in MOFs. In this communication, we present the synthesis, structure and magnetic behavior of **I**.‡

The asymmetric unit of **I** consists of two independent Mn^{2+} ions and one trimellitate anion. While Mn(1) is in a general position, Mn(2) lies on an inversion centre with a site multiplicity of 0.5. Though both of the Mn^{2+} ions are hexa coordinated, the Mn(1) has distorted trigonal prismatic geometry and Mn(2) has an octahedral geometry with carboxylate oxygen atoms (Fig. 1a). The Mn(2)O₆ octahedral units are connected with two Mn(1)O₆ trigonal prismatic units *via* two different μ₃ carboxylate oxygen atoms (O(3) and O(4)) and two Mn(1)O₆ units are connected *via* O(5) μ₃ carboxylate oxygen
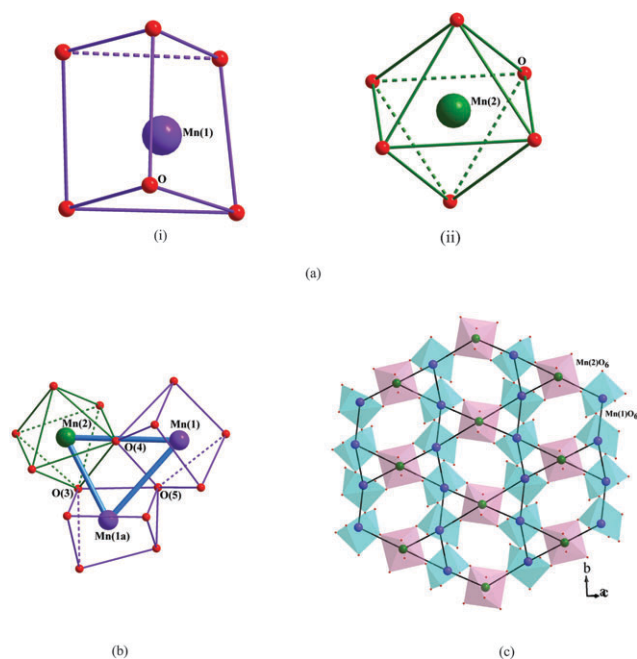

Fig. 1 (a) The octahedral (i) and trigonal prismatic geometry (ii) of Mn^{2+} ions in **I**, (b) the structure of the triangular unit formed by the connectivity of two Mn(1)²⁺ and one Mn(2)²⁺ ions, and (c) a polyhedral view of the Kagome layer formed by the connectivity of Mn(1)O₆ and Mn(2)O₆ polyhedral units.

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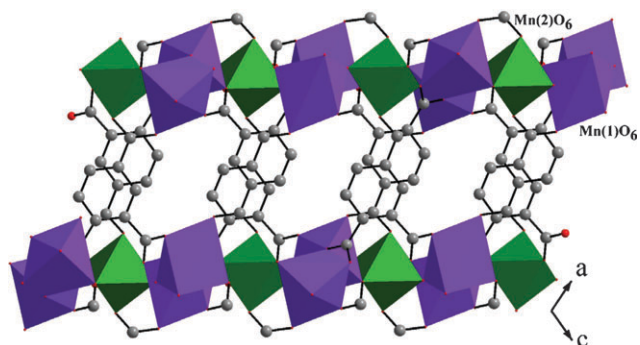
Fig. 2 The connectivity between the Kagome layers in **I** through 1,2,4-BTC units.

Fig. 3 (a) Plot of $\chi_M T$ vs. T ($H = 1000$ Oe) (FC). Inset shows the $1/\chi_M$ vs. T plot, (b) field cooled (FC) and zero-field cooled (ZFC) plot of χ_M vs. T at $H = 50$ Oe, (c) $\chi_M T$ vs. T plot at various fields, (d) M vs. H plot at 5 K

atom (μ_3-O connects one carbon and two Mn) forming a triangular lattice (Fig. 1b), which are connected through the corners to form a layer that resembles the Kagome arrangement (Fig. 1c). Topologically, the distorted Kagome layer can be considered as a 4-connected node with $3^2 6^2$ net. A careful examination of the triangular arrangement of the metal ions in **I** indicates three distinct Mn–Mn distances and Mn–O–Mn angles: 3.36, 3.8 and 4.1 Å; 97.88, 130.53 and 112.28°. The Mn–Mn connectivity within the layer shows that each of the triangles within the layer is formed by two Mn(1) and one Mn(2) species (Fig. 1c). The benzene carboxylate units connect the layers three-dimensionally (Fig. 2).

The magnetic studies carried out on **I** are shown in Fig. 3. At RT, the effective magnetic moment (μ_{eff}) is 6.01 μ_B. The $\chi_M T$ versus T curve is shown in Fig. 3a. The $\chi_M T$ value decreases continuously with decreasing temperature and reaches a minimum of 2.59 emu mol^{-1} K at 23 K. On cooling further $\chi_M T$ increases rapidly suggesting that the magnetic behavior at low temperature should be either ferrimagnetic or canted antiferromagnetic.[10] The $1/\chi_M$ vs. T curve is shown as the inset of Fig. 3a. Above 100 K, the magnetic behavior can be fitted by the Curie–Weiss law, with $C = 5.35$ emu mol^{-1} and $\theta_P = -46.1$ K. The negative θ_P indicates antiferromagnetic coupling between the Mn^{+2} ions. The field-cooled (FC) and zero-field-cooled (ZFC) magnetizations measured at 50 Oe down to 2 K, indicate a deviation at 13 K. AC magnetic susceptibility studies indicate (see ESI†) a sharp peak suggesting a transition with a critical temperature $T_c \approx 13$ K. The degree of frustration, f, defined as θ_P/T_c,[11] was found to be 3.55, which is far lower than that observed in the classical Kagome lattice of iron jarosite.[12] The field-cooled $\chi_M T$ values at different applied fields as a function of temperature show a spontaneous increase around 13 K, which is more noticeable for lower field strengths (Fig. 3c). The drop in $\chi_M T$ below 13 K may be due to the magnetic field saturation effect.[10] The field dependence of the magnetization, M vs. H (0–50 kOe) at 5 K (Fig. 3d), shows behavior typical of a canted antiferromagnet with a sharp increase of the magnetization at low fields and a linear variation of M at $H > 20$ kOe.[13] At 50 kOe the magnetization value reaches 1.57 μ_B, a value that is far below the saturation value of 5.92 μ_B expected for a spin-only Mn^{2+} ion. This lack of saturation at high field confirms that the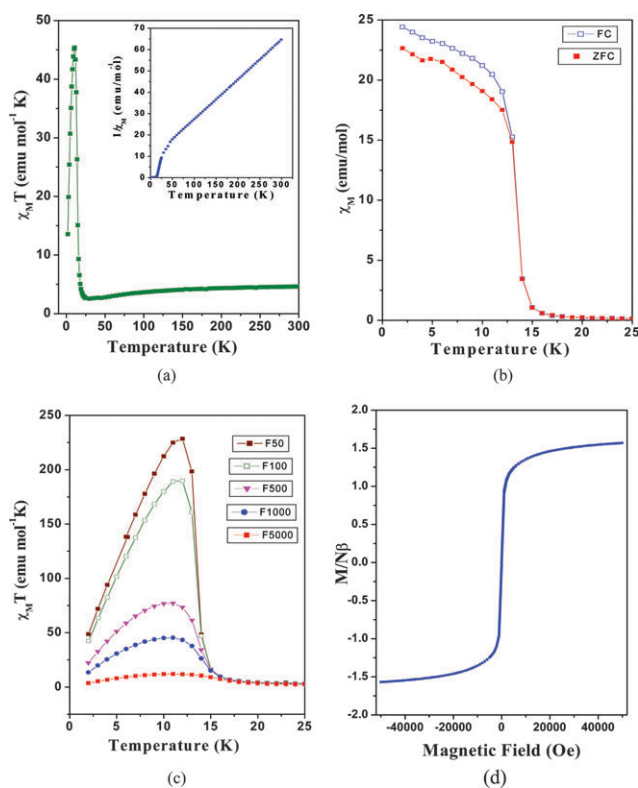 low temperature magnetic ground state is a canted antiferromagnetic one,[14] which is due to the spin canting caused by the antisymmetric Dzyaloshinsky–Moriya (DM) exchange.

Taking into account the structural features of this compound, further inspection of the magnetic behavior is worthwhile to understand the smaller frustration and the origin of the DM interaction. The recent reports of Mn^{2+} carboxylates, [Mn{Mn$_3$(μ_3-F)(bta)$_3$(H$_2$O)$_6$}] and [Mn$_2$(THFTC)(H$_2$O)$_3$], with triangular arrangements of the Mn^{2+} ions show no long range ordering.[15] The manganese carboxylate, [Mn$_3$\{C$_6$H$_3$(COO)$_3$\}$_2$], with an isolated linear Mn$_3$ unit connected through trimesate anions show simple antiferromagnetic behavior through intra- and inter-trimer interactions.[16] In all these compounds Mn^{2+} ions are exclusively present in octahedral coordination. In the present compound, however, Mn^{2+} ions are in trigonal prismatic and octahedral geometry (Fig. 1a). Antiferromagnetic interactions between the Mn and O atom occurs through the super exchange process using metal d orbitals and oxygen p orbitals. The octahedral geometry [Mn(2)] is more favorable for overlap between the p orbitals of oxygens and $d_{x^2-y^2}$ and d_{z^2} orbitals of the Mn^{2+} ions. In the trigonal prismatic geometry [Mn(1)], the overlap is between the d_{xz} and d_{yz} orbitals of Mn^{2+} and the p orbitals of oxygen.[17] This difference in the super exchange pathway between the Mn^{2+} ions via the oxygens can give rise to a large antisymmetric DM interaction, which is responsible for the spin canting in our structure.[2c,3d,18] This geometric

difference between the Mn^{2+} ions (in particular, the different Mn–Mn distances and angles mentioned above) reduces the frustration within the triangular lattice and at the same time both the in-plane and out-of-plane DM vectors would be nonzero in this system, with the in-plane component inducing canted spin moments in the out-of-plane directions resulting in long range ordering in **I**. The inter-layer distance in **I** is ∼8 Å, which suggests that the magnetic interactions are confined within the layers.

In summary, $[Mn_3\{C_6H_3(COO)_3\}_2]$ represents first single atom bridged Kagome related layer in a three-dimensional MOF compound formed by two geometrically different Mn^{2+} species. The presence of the trigonal prismatic and octahedrally coordinated Mn^{2+} ions reduces the frustration giving rise to canted antiferromagnetism through antisymmetric Dzyaloshinsky–Moriya (DM) exchange.

Notes and references

‡ A mixture of $Mn(OAc)_2 \cdot 4H_2O$: 1,2,4-tricarboxylic acid : imidazole : KOH/LiOH : water (1 : 1 : 1 : 2 : 444) was reacted in a PTFE-lined acid digestion vessel (23 mL) at 220 °C for 24 h. Colorless rectangular crystals of **I** were collected (yield ≈ 70%) after washing with a sufficient quantity of water and diethyl ether. The starting pH value and the pH value after the reaction were 6 and 4.5, respectively. Anal. Calcd for **I**: C, 37.30; H, 1.04. Found: C, 37.12; H, 1.11. The compound was characterized by IR, TGA and EPR spectroscopic studies. The structure was determined using a Bruker AXS smart Apex CCD diffractometer at 293(2) K. The structure was solved and refined using SHELXL97 present in the WinGx suite of programs (Version 1.63.04a). Crystal data for **I**: $[Mn_3\{C_6H_3(COO)_3\}_2]$, $M = 579.04$, monoclinic, space group $P2_1/n$ (no. 14), $a = 11.314(3)$, $b = 6.5962(16)$, $c = 11.391(3)$ Å, $\beta = 111.029(4)$; $V = 793.5(3)$ Å^3, $Z = 2$, $\rho_{cal} = 2.424$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 2.435$ mm^{-1}, 6663 reflections, 1853 unique ($R_{int} = 0.03$), 1600 observed $I > 2\sigma(I)$, $R_1 = 0.0425$, w$R_2 = 0.0714$ and GOF = 1.089 for 151 parameters. CCDC 637648. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b715314g

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