

Novel frustrated magnetic lattice based on triangular $[\text{Mn}_3(\mu_3\text{-F})]$ clusters with tetrazole ligands†

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Unprecedented $[\text{Mn}^{\text{II}}_3(\mu_3\text{-F})(\mu\text{-N-N})_3]$ triangular clusters with tetrazole ligands are linked by Mn^{II} ions to generate a novel spin-frustrated 2D lattice exhibiting antiferromagnetic ordering.

Geometrically frustrated magnetic materials (GFMs) have attracted much attention in solid state science over the past few years, because the competing interactions in these materials can suppress or significantly reduce long-range magnetic ordering, and may induce unusual ground-state behaviors such as spin glasses, spin liquids and spin ices.¹ Although not always appreciated, the effects of magnetic frustration are inherent in many magnetic lattices based on triangular or tetrahedral “plaquettes”, and the most extensively studied lattices are the 2D triangular and kagome lattices and the 3D fcc (face-centred cubic) and pyrochlore lattices, in which the plaquettes share corners, edges or faces.^{1–3} While most model lattices studied to date have been based on inorganic oxides and salts, an alternative approach to GFMs is emerging, which utilizes the geometric and electronic preference of selected organic ligands and metal ions (or clusters) to produce metal–organic networks.⁴ This approach may provide model systems that show weaker interactions with tunable structures and magnetic behaviors, and may also present new opportunities to obtain GFMs with new lattice topologies or new functions.^{5,6} However, the examples of this approach are still rare, and there is much to be explored.

Since the triangular arrangement of three spins with antiferromagnetic (AF) coupling is the simplest archetype of spin frustration, a rational concept is to use triangular clusters as the secondary building units for frustrated lattices. In fact, in the domain of coordination chemistry, transition metal clusters with the triangular $[\text{M}_3(\mu_3\text{-X})]$ motifs (X = O, OH, or very rarely, F) have been extensively investigated for their structures, electron transfer properties, catalytic activities, or biological relevance, in addition to the magnetic properties.^{7–9} They have also been used to build microporous metal–organic frameworks.¹⁰ The triangular motifs are usually stabilized by carboxylate bridges or by the N–N bridges from pyrazolate or triazolate ligands. The effectiveness of the azolate ligands to form triangular clusters of the type $[\text{M}_3(\mu_3\text{-X})(\text{N-N})_3]$ encourages us to investigate the tetrazolate

ligands, which possess additional N-donor sites for network formation. To our knowledge, $[\text{M}_3(\mu_3\text{-X})]$ compounds with tetrazolate ligands have not yet been reported. Here we describe a manganese(II) complex with bis(5-tetrazolyl)amine (H_2bta), $[\text{Mn}\{\text{Mn}_3(\mu_3\text{-F})(\text{bta})_3(\text{H}_2\text{O})_6\}_2]$ (**1**). The compound exhibits a novel 2D frustrated lattice with alternating triangular motifs and mononuclear centers, and according to magnetic studies, it behaves as a low-temperature antiferromagnet.

The hydrothermal reaction of MnCl_2 , $\text{Na}[\text{N}(\text{CN})_2]$ and NaN_3 in the presence of excess KF yielded crystals of **1** in good yield. The bta^{2-} ligand was generated *in situ* from the dicyanamide and azide ions. The *in situ* formation of tetrazoles *via* [2 + 3] cycloaddition reaction of azide and nitriles has been well established for the syntheses of various coordination compounds.¹¹ The presence of F^- in **1** is confirmed by X-ray crystallography and analytic data including that for F.‡

Single crystal X-ray analyses§ showed that compound **1** is a 2D coordination polymer built from trinuclear $[\text{Mn}_3(\mu_3\text{-F})]$ clusters and mononuclear Mn(II) centers (Fig. 1). There are two

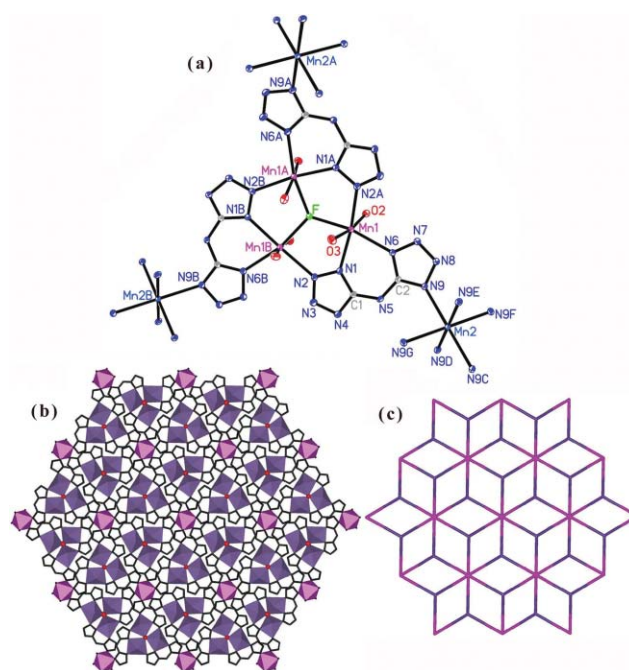


Fig. 1 Views of the structure of **1**, showing (a) coordination environments of the metal ion and the ligand, (b) the 2D layer, and (c) the 3,6-connected net of the layer. Symmetry codes: A, $-y + 1, x - y + 1, z$; B, $-x + y, -x + 1, z$; C, $-x + 2, -y + 2, -z + 1$; D, $-y + 2, x - y + 1, z$; E, $-y, -x + y + 1, -z + 1$; F, $-x + y + 1, -x + 2, z$; G, $x - y + 1, x, -z + 1$.

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independent sets of Mn(II) ions (Mn1 and Mn2). Each Mn1 ion assumes a pseudo-octahedral $[\text{MnFN}_3\text{O}_2]$ coordination geometry, with the Mn–N/F/O distances ranging from 2.1798(16) to 2.3025(14) Å. The equatorial positions are occupied by a fluoride ion and three nitrogen atoms (N1, N6 and N2A) from two bta^{2-} ligands, and the axial positions are occupied by two water molecules (O2 and O3). The fluoride ion resides on a threefold axis, and acts as a μ_3 bridge linking three equivalent Mn1 ions, generating an equilateral triangle with the literal Mn \cdots Mn distances equal to 3.7700(8) Å. The Mn–F–Mn bridging angle is 118.61(2)°, and the fluoride ion is displaced out of the Mn₃ plane by 0.261(2) Å, defining a very flattened pyramidal shape for the $[\text{Mn}_3(\mu_3\text{-F})]$ cluster. The cluster is surrounded by three identical bta^{2-} ligands, each of which ligates a Mn1 ion *via* two nitrogens (N1 and N6) from different tetrazole rings and sets up a N–N bridge between two Mn1 ions *via* two neighboring nitrogens (N1 and N2) from one tetrazole ring. The ligand is also bonded to a Mn2 ion through N9, and hence constitutes a 1,5-tetrazole bridge between Mn1 and Mn2 with a Mn \cdots Mn distance of 6.598(1) Å. The Mn2 ion resides at the crystallographic -3 position and adopts the octahedral coordination geometry with six N9 atoms. Thus, each Mn2 is linked to six Mn₃ clusters, and each cluster is connected to three Mn2 centers, generating an infinite 2D layer parallel to the *ab* plane. Taking the clusters as 3-connected nodes and the Mn2 centers as 6-connected nodes, the layer represents a novel type of 3,6-connected 2D net, $(4^3)_2(4^66^68^3)$ (Fig. 1c). Due to the octahedral geometry of Mn2, the layer is doubly decked (Fig. 2), with the decks being defined by the $[\text{Mn}_3(\mu_3\text{-F})(\text{bta})_3]$ moieties and linked by Mn2.

The coordinated water molecules and the bta^{2-} ligands provide a rich store of donor and acceptor sites for intra- and interlayer hydrogen bonding (Fig. 2, see ESI for structural parameters†). Within each $[\text{Mn}_3(\mu_3\text{-F})(\text{bta})_3(\text{H}_2\text{O})_3]$ moiety, the three equivalent O3 water molecules form three O3–H \cdots O3' hydrogen bonds, generating a triangular ring with graph set $\text{R}_3^3(6)$. The remaining hydrogen atom of the O3 water molecule is involved in intralayer O–H \cdots N hydrogen bonding with a tetrazole N4 atom. The third type of intralayer hydrogen bonds are the N–H \cdots N interactions involving the amine N5–H groups and the tetrazole N7 atoms from different trinuclear moieties. For interlayer interactions, each coordinated O2 water molecule forms two O–H \cdots N hydrogen bonds with two tetrazole nitrogens (N3 and N8) from an adjacent layer. These hydrogen bonds lead to a relatively close packing of the layers, and the nearest interlayer Mn \cdots Mn distances are

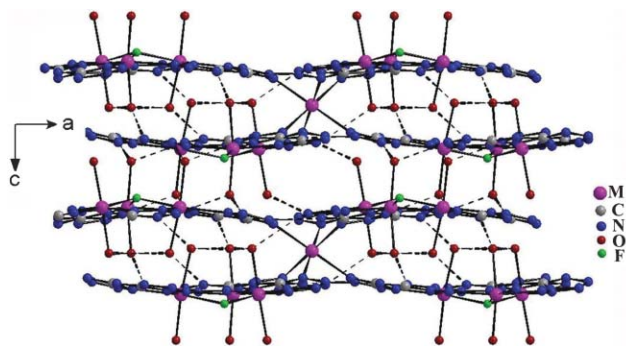


Fig. 2 A view of the packing of the layers showing both intra- and interlayer hydrogen bonds.

6.853(3) Å for Mn2 \cdots Mn2(*y*, *x*, 0.5 – *z*) and 6.998(3) Å for Mn1 \cdots Mn1(*x*, *x* – *y* + 1, *z* – 0.5), which are comparable with the intralayer Mn1 \cdots Mn2 distance spanned by the tetrazole ring.

From a structural viewpoint, compound **1** displays several novel features that are worth noting. It represents the first compound containing the $[\text{Mn}^{\text{II}}_3(\mu_3\text{-F})]$ motif. It is the first $[\text{M}_3(\mu_3\text{-X})]$ species with tetrazole ligands, and the 3,6-connected 2D net topology is also unprecedented. More importantly, the combination of the net topology and the cluster geometry leads to a novel 2D frustrated lattice (see below).

The magnetic susceptibility of **1** was measured in the 2–300 K range at 1 kOe (Fig. 3a). The χT value per formula at 300 K is 29.75 emu K mol^{–1}, close to the spin-only value (30.63 emu K mol^{–1}) expected for seven magnetically isolated high-spin Mn(II) ions with *g* = 2.00. As the temperature is lowered, χT decreases more and more rapidly to 2.69 emu K mol^{–1} at 2 K and tends to vanish further, and χ first increases and then decreases, with a maximum of 1.36 emu mol^{–1} at 2.5 K. The χ^{-1} vs. *T* plot above 10 K is exactly linear, following the Curie–Weiss law with *C* = 31.9 emu K mol^{–1} and θ = –22.1 K. These features clearly indicate AF interactions between Mn(II) ions. The drop of χ below 2.5 K, verified further by zero-field-cooled (ZFC) and field-cooled (FC) behaviors at 20 Oe (Fig. 3a, inset), suggests the onset of long-range AF ordering below *T*_N = 2.5 K. This is also supported by the field-dependent magnetization measured at 2 K (Fig. 3b): the magnetization increases linearly with the field, and the value at 50 kOe is far from saturation.

Taking into account the structural features of the compound, further inspection of the magnetic behaviors is worthwhile. An equilateral triangle of three antiferromagnetically coupled spins is inherently frustrated. In the present compound, frustrated Mn^{II}₃ triangles are linked by 6-connected mononuclear Mn(II) ions. The resulting 2D lattice (Fig. 3c) represents a novel type of frustrated lattice, and it is distinct from other geometrically frustrated 2D lattices, where the triangles share corners and edges, as in the

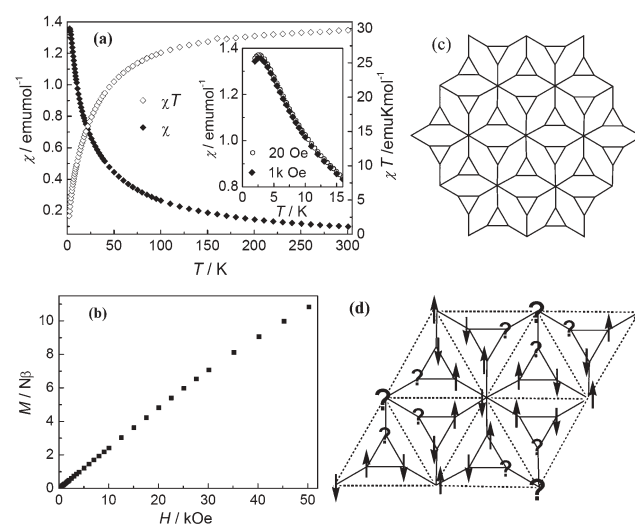


Fig. 3 (a) Temperature dependence of the susceptibility of **1** at 1 kOe. Inset: FC (20 and 1000 Oe) and ZFC (20 Oe) plots. (b) Field-dependent magnetization at 2 K. (c) Schematic illustration of the 2D lattice. (d) A segment of the lattice illustrating the frustration and the triangular sublattice (\cdots) of Mn2.

well-known triangular and kagome lattices, or are linked by diamagnetic bridges, as in the bounce and star lattices.^{1d} In this new lattice, spin frustration may also occur on the mononuclear Mn(II) center, which is surrounded and antiferromagnetically coupled by six frustrated triangles, as schematized in Fig. 3d. It is interesting to note that the sublattice of the mononuclear centers exhibits the triangular topology (Fig. 3d, ...). The novel lattice pattern is also aesthetically intriguing. It is based on six-petaled flower-like motifs, and each flower shares its petals with six neighbouring flowers (Fig. 3c).

Frustration in an equilateral triangle of three half-integer spins generates an orbitally degenerate ground state with $S = 1/2$.¹² The stoichiometry and connecting mode of the mono- and trinuclear moieties in the present 2D lattice would lead to an uncompensated spin moment, which would cause a rise in χ_M at low temperature. The observed low-temperature drop in χ_M for **1** suggests that the net spin moment is suppressed by interlayer AF interactions, which lead to 3D AF ordering below $T_N = 2.5$ K. This is consistent with the relatively close packing of the layers in **1**. It has been stated that magnetic frustration can suppress or significantly reduce long-range ordering. Experimentally, the degree of frustration in an antiferromagnet is identified by the ratio of the Weiss constant to the ordering temperature, $f = |\theta|/T_N$.¹ The ratio deviates much from 1 for a frustrated system, in contrast to a non-frustrated 3D ordering system where $T_N \sim |\theta|$. For compound **1**, the relatively large ratio ($f = 8.9$) is consistent with the presence of frustration.

In conclusion, we have described a molecular-based antiferromagnet with an unusual 2D frustrated lattice, in which the unprecedented $[\text{Mn}^{\text{II}}_3(\mu_3\text{-F})(\mu_2\text{-N-N})_3]$ triangular clusters are separated by mononuclear Mn(II) ions. The lattice topology implies an inherent net spin moment, which is suppressed by interlayer AF ordering in the present case. Therefore, different bulk behaviors may be expected, if the water molecules on the layer surface are substituted to tune or reduce the interlayer interactions.^{5b} Investigations facing this challenge are being attempted in our lab.

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Notes and references

‡ Synthesis: a mixture of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (119 mg, 0.6 mmol), $\text{NaN}(\text{CN})_2$ (35.6 mg, 0.4 mmol), KF (58.1 mg, 1.0 mmol) and NaN_3 (0.052 g, 0.8 mmol) in H_2O (5 mL) was stirred for 10 min in air, sealed in a Teflon-lined reactor, heated at 115 °C for 3 days, and then cooled to room temperature slowly. Colorless polyhedral crystals of **1** were obtained and collected by filtration. Yield, 89%. Anal. Calcd for $\text{C}_{12}\text{H}_{30}\text{Mn}_7\text{N}_{54}\text{O}_{12}\text{F}_2$: C, 9.3; H, 2.0; N, 49.0; F, 2.5. Found: C, 9.7; H, 2.3; N, 49.5; F, 2.3%. Main IR bands (KBr): **1**, 3525 s, 3262 s, 3157 s, 3050 s, 2919 s, 1630 vs, 1545 w, 1517 vs, 1429 m, 1319 m, 1265 m, 1182 m, 1147 m, 1125 w, 1097 w, 1036 w, 1011 w, 863 m, 800 m, 745 m, 676 m, 600 m.

§ Crystal data: for **1**, $\text{C}_{12}\text{H}_{30}\text{Mn}_7\text{N}_{54}\text{O}_{12}\text{F}_2$, $M_r = 1545.48$, trigonal, space group $P\bar{3}c1$, $a = 14.355(3)$ Å, $c = 13.705(5)$ Å, $V = 2445.7(12)$ Å³, $Z = 2$,

$\mu(\text{Mo K}\alpha) = 1.868 \text{ mm}^{-1}$, $\rho_{\text{calcd}} = 2.099 \text{ g cm}^{-3}$, $T = 293 \text{ K}$, $S = 1.091$, $R1 = 0.0277$ for 1805 observed reflections with $I > 2\sigma(I)$, and $wR2 = 0.0669$ for 1946 independent reflections. CCDC 634263. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b701840a

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