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Two-dimensional frameworks built from Single-Molecule Magnets

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Keywords:

networks; complexes; clusters; family; dimer; units

Abstract

Fine tuning the Mn / salicylaldoxime / trimesic acid reaction conditions leads to the formation of a regular 2D net held together by dative bonds and to a non-regular 2D net stabilised by both dative and hydrogen bonds. Both networks are built from [Mn₆] Single-Molecule Magnets.

Introduction

Since it has been established that the physical properties of crystalline molecular materials can be influenced by crystal packing effects and intermolecular interactions (*e.g.* hydrogen bonding, $\pi \cdots \pi$ interactions *etc.*), we and others have been investigating how to manipulate the magnetic properties of Single-Molecule Magnets (SMMs) in the solid state by modulating their surroundings.¹ To this end, we recently exploited certain members of a family of hexanuclear, [Mn₆], and trinuclear, [Mn₃], Mn^{III} complexes of general formulae [Mn^{III}₆O₂(R-sao)₆(O₂CR)₂(L)₄·6] and [Mn^{III}₃O(R-sao)₃(X)(L)₃] (saoH₂ = salicylaldoxime; R = H, Me, Et *etc.*; X = RCO₂⁻, ClO₄⁻; L = solvent)²⁻³ as building blocks for constructing discrete and infinite supramolecular architectures with the use of both bis-pyridyl⁴ and bis-carboxylate⁵ type ligands. Both types of bridging ligands resulted in, among others, coordination polymers built from either [Mn₃] or [Mn₆] clusters. The bis-pyridyl type ligands gave rise to both one- (1D) and two-dimensional (2D) coordination polymers based on [Mn₃] SMMs while the bis-carboxylate ligands resulted in 1D coordination polymers incorporating [Mn₆] SMMs.^{4,5}

Having in mind that the incorporation of bis-carboxylate ligands resulted in polymeric species where the [Mn₆] clusters retained their single molecule behaviour, we sought to construct higher dimensionality coordination polymers (*i.e.* 2D or 3D) built from [Mn₆] SMMs and polycarboxylate ligands. For this purpose, we incorporated 1,3,5-benzene-tricarboxylic acid (trimesic acid, tmaH₃) into blends of manganese / saoH₂ reaction mixtures to isolate the 1D coordination polymer [Mn₆O₂(sao)₆(tmaH)(MeOH)_{8.5}(H₂O)_{0.5}]·(MeOH)_{0.75}(H₂O)_{0.125} **1**·(MeOH)_{0.75}(H₂O)_{0.125} and the 2D coordination polymer [Mn₆O₂(sao)₆(tma)_{0.66}(MeOH)_{3.33}(H₂O)_{1.33}]·(MeOH)_{4.46}(H₂O) **2**·(MeOH)_{4.46}(H₂O). Both polymers are constructed from [Mn₆] SMM building blocks. Besides the efforts to intentionally link SMMs or magnetically interesting clusters, higher dimensionality (*i.e.* 2D, 3D) polymers are scarce.⁶ Complex **2** represents a rare 2D framework constructed intentionally from SMMs building blocks.

Although it is possible to employ pre-formed [Mn₆] and [Mn₃] species as starting materials for the synthesis of polymeric materials [they are solution stable as gauged by NMR, mass

spectrometry and solution SQUID magnetometry⁷], it is much more efficient to simply perform the reactions *in situ*. The $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ / saoH_2 / tmaH_3 / base reaction blend is however very sensitive to reaction conditions and indeed it produces different complexes depending on the order of addition of the reagents. The 1D coordination polymer **1** is produced when tmaH_3 is added into an alcoholic solution containing $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ / saoH_2 / MeONa , while the 2D coordination polymer **2** is formed when MeONa was added into an alcoholic solution containing $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ / saoH_2 / tmaH_3 . Complex **1** was isolated serendipitously during our efforts to synthesise the targeted 2D coordination polymer **2**.

Complex **1** (Figure 1) crystallises in the triclinic space group $P\bar{1}$.[‡] The asymmetric unit consists of two tmaH^{2-} anions, one $[\text{Mn}^{\text{III}}_6]$ and two $[\text{Mn}^{\text{III}}_3]$ units.[†] In effect, there are two crystallographically independent $[\text{Mn}_6]$ clusters, namely $[\text{Mn}_6]_{\text{A}}$ and $[\text{Mn}_6]_{\text{B}}$, repeating along the chain of **1**. Each $[\text{Mn}_6]$ unit consists of two off-set, stacked $[\text{Mn}^{\text{III}}_3\text{O}(\text{sao})_3]^+$ triangles linked by two oximate O-atoms, while one phenolato O-atom bridges between the $[\text{Mn}_3]$ subunits in $[\text{Mn}_6]_{\text{A}}$. Four sao^{2-} ligands bridge along the edges of the $[\text{Mn}_3]$ subunits in a $\mu_3:\eta^1:\eta^1:\eta^2$ fashion, one in a $\mu_3:\eta^2:\eta^1:\eta^1$ fashion while the remaining seven sao^{2-} ligands adopt the $\mu:\eta^1:\eta^1:\eta^1$ coordination mode. Ten out of the twelve crystallographically independent Mn^{III} atoms are in an (axially) elongated octahedral environment with one Mn^{III} in each of the $[\text{Mn}_6]$ clusters being five-coordinate and in a square pyramidal environment. Nine MeOH molecules (one is 50% disordered with a H_2O molecule) occupy the Jahn Teller positions on the Mn^{III} ions, with the remaining sites coordinated by carboxylato O-atoms from the two crystallographically independent tmaH^{2-} ligands. These ligands adopt the $\mu_4:\eta^1:\eta^1:\eta^1:\eta^1$ and $\mu_3:\eta^1:\eta^1:\eta^1$ coordination modes, respectively. The Mn-N-O-Mn torsion angles for $[\text{Mn}_6]_{\text{A}}$ are 32.55° for Mn4-N-O-Mn5, 38.22° for Mn5-N-O-Mn6, 21.47° for Mn6-N-O-Mn4, 41.83° for Mn7-N-O-Mn8, 12.25° for Mn8-N-O-Mn9 and 30.13° for Mn9-N-O-Mn7. For $[\text{Mn}_6]_{\text{B}}$ the corresponding angles are 18.00° for Mn1-N-O-Mn2, 8.18° for Mn2-N-O-Mn3, 13.44° for Mn3-N-O-Mn1, 15.99° for Mn10-N-O-Mn11, 9.05° for Mn11-N-O-Mn12 and 18.44° for Mn12-N-O-Mn10.

(turn to next page →)

Figure 1. (top) The asymmetric unit of complex **1**. (bottom) The hydrogen-bonded chains of complex **1** creating a non-regular 2D framework. Most hydrogen atoms and some carbon atoms of the sao^{2-} ligands have been omitted for clarity. Colour code: Mn: purple, O: red, N: blue, C: grey, H: cyan.

The chains of **1** are arranged in parallel, with the free carboxylic acid groups of the tmaH^{2-} ligands able to donate a hydrogen bond to a phenolato O-atom and accept a hydrogen bond from a neighbouring coordinated MeOH molecule, thus bridging between chains to create a 2D non-regular network (Fig. 1) with vertex symbol $(4.6^2; 4.6.4.6)$. The tmaH^{2-} ligands and the $[\text{Mn}_6]_{\text{B}}$ clusters serve as 3- and 4-connected nodes within the 2D network, respectively, with $[\text{Mn}_6]_{\text{A}}$ simply bridging between the tmaH^{2-} ligands.

Complex **2** also crystallises in the triclinic space group $P\bar{1}$.[‡] The asymmetric unit consists of one tma^{3-} anion and three $[\text{Mn}^{\text{III}}_3\text{O}(\text{sao})_3]^+$ subunits (Fig. 2).[†] This arrangement gives rise to three crystallographically independent $[\text{Mn}_6]$ clusters, with each sitting on an inversion centre. Two off-set stacked $[\text{Mn}^{\text{III}}_3\text{O}(\text{sao})_3]^+$ triangles linked by two oximato O-atoms create each $[\text{Mn}_6]$ cluster. Therefore, four sao^{2-} ligands bridge along the edges of the $[\text{Mn}_3]$ subunits in a $\mu_3:\eta^1:\eta^1:\eta^1$ fashion, while two sao^{2-} ligands adopt the $\mu_3:\eta^1:\eta^1:\eta^2$ coordination mode. Two Mn^{III} ions in each $[\text{Mn}_6]$ are five-coordinate in a square pyramidal environment while the remaining four Mn^{III} ions are in an (axially) elongated octahedral environment. Ten MeOH and four H_2O molecules, ten carboxylate O-atoms from the tma^{3-} ligands and six oximato O-atoms from the sao^{2-} ligands

occupy the Jahn Teller positions on the Mn^{III} ions. The tma^{3-} ligand bridges five Mn^{III} ions, from three different $[\text{Mn}_6]$ clusters, adopting the $\mu_5:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1$ coordination mode. The Mn-N-O-Mn torsion angles are 9.45° for Mn1-N-O-Mn2, 1.81° for Mn2-N-O-Mn3 and 31.37° for Mn3-N-O-Mn1 for the first $[\text{Mn}_6]$, 24.64° for Mn4-N-O-Mn5, 14.67° for Mn5-N-O-Mn6 and 18.22° for Mn6-N-O-Mn4 for the second $[\text{Mn}_6]$ and 2.33° for Mn7-N-O-Mn8, 29.81° for Mn8-N-O-Mn9 and 22.60° for Mn9-N-O-Mn7 for the third $[\text{Mn}_6]$.

The $[\text{Mn}_6]$ clusters and the tma^{3-} ligands assemble to create a regular 2D network with a (6,3) topology, commonly known as a honeycomb, with the tma^{3-} ligands serving as 3-connected nodes and the $[\text{Mn}_6]$ clusters as the spacers (Fig. 2).

Figure 2. (top) The asymmetric unit of complex **2**. (bottom) The 2D framework of complex **2**. All hydrogen atoms and many carbon atoms of the sao^{2-} ligands have been omitted for clarity. Colour code as in Figure 1.

Previous studies of molecular salicylaldoxime-based $[\text{Mn}^{\text{III}}_6]$ and $[\text{Mn}^{\text{III}}_3]$ clusters have shown that their magnetic behaviour is strongly correlated to small geometrical changes. Specifically, the sign and magnitude of the exchange (J) between neighbouring Mn^{III} ions is dependent on the Mn-N-O-Mn torsion angle. Unfortunately the presence of more than one crystallographically independent $[\text{Mn}_6]$ in the crystal structures of both **1** and **2**, which possess different geometries, precludes a detailed *quantitative* analysis of the magnetic behaviour.

Solid state dc magnetic susceptibility data for **1** and **2** were recorded between 275 and 5 K in an applied field of 0.1 T. The plots of $\chi_{\text{M}}T$ versus T for **1** and **2** are shown in Fig. S1. The $\chi_{\text{M}}T$ products at 275 K are 16.54 and 14.95 $\text{cm}^3 \text{mol}^{-1} \text{K}$ for **1** and **2**, respectively, close to the spin-only ($g = 2$) value of 18 $\text{cm}^3 \text{mol}^{-1} \text{K}$ expected for a $[\text{Mn}_6]$ unit comprising six high spin Mn^{III} ions. The $\chi_{\text{M}}T$ values for both complexes remain approximately constant as the temperature is lowered, before dropping more rapidly at temperatures below 125 K. Thereafter, the $\chi_{\text{M}}T$ value for complex **1** decreases constantly to reach a value of 9.1 $\text{cm}^3 \text{mol}^{-1} \text{K}$ at 5 K, while that for complex **2** decreases to a value of $\sim 8.0 \text{ cm}^3 \text{mol}^{-1} \text{K}$ at 20 K and then plateaus to 5 K. The decrease of the $\chi_{\text{M}}T$ product upon cooling to smaller but non-zero values is consistent with the presence of both antiferromagnetic and ferromagnetic interactions between the Mn^{III} ions with the low-temperature values indicating $S \approx 4$ spin ground states for the $[\text{Mn}^{\text{III}}_6]$ units in both complexes. Indeed we note that the $\chi_{\text{M}}T$ behaviour for **1** and **2** is very similar to that observed for previously reported and magnetically isolated $[\text{Mn}^{\text{III}}_6]$ complexes with $S = 4$ spin ground states. For comparison we include in Figure S1 the data for $[\text{Mn}_6\text{O}_2(\text{sao})_6(\text{ketoacetate})_2(\text{EtOH})_2(\text{H}_2\text{O})_2]$ (**3**) and $[\text{Mn}_6\text{O}_2(\text{sao})_6(1\text{-Me-cyclohex})_2(\text{MeOH})_4]$ (**4**) from reference 3c which contain $[\text{Mn}_6]$ with similar Mn-N-O-Mn torsion angles. In order to investigate the possibility of long range antiferromagnetism we performed zero field ac susceptibility measurements on **1** and **2** in the 1.8 – 10 K temperature range with a 3.5 G ac field oscillating at frequencies ranging from 50 – 1000 Hz (Fig. 3). A cusp in the real component χ' (Fig. S3) is accompanied by a non-zero imaginary component χ'' at ~ 3 K. The maxima for both are strongly frequency dependent, suggesting super-paramagnetic blocking of the magnetisation. Arrhenius plots (inset Fig. 3) constructed from the χ'' data afford $\tau_0 = 3.3 \times 10^{-9} \text{ s}$ and $U_{\text{eff}} = 32.84 \text{ K}$ (22.82 cm^{-1}) for **1**, and $\tau_0 = 5.6 \times 10^{-8} \text{ s}$ and $U_{\text{eff}} = 24.54 \text{ K}$ (17.05 cm^{-1}) for **2**. The presence of *significant* inter- $[\text{Mn}_6]$ interactions would be expected to slow down the spin dynamics at low temperatures and this would be manifested in a smaller frequency shift, k . Using the average values of blocking temperatures (T_{B}) of 2.70 K for **1** and 2.69 K for **2**, the frequency shift of T_{B} is calculated as $k = \Delta T_{\text{B}} / (T_{\text{B}} \Delta \log f)$, where ΔT_{B} is the change in T_{B} for the given change in frequency $\Delta \log f$, where $\Delta \log f = 1.30$ for both complexes. This provides values of 0.19 and 0.24 for **1** and **2**, respectively, which are within the range expected for super-paramagnets and close to those reported for molecular $[\text{Mn}_6]$ complexes. This suggests that the relaxation is in accordance with SMM behavior, and is not attributed to long

range interactions mediated through the polycarboxylate ligands.

Figure 3. Plot of χ'' versus T for complex **1** at the indicated temperature and frequency ranges. Inset: Arrhenius plot constructed from the χ'' data to afford $\tau_0 = 3.3 \times 10^{-9}$ s and $U_{\text{eff}} \approx 33$ K.

To conclude, we presented two new coordination polymers built from $[\text{Mn}_6]$ clusters and trimesate anions. The first polymer conforms to a non-regular 2D net held by both dative and hydrogen bonds, while the second adopts a regular 2D net held together exclusively by dative bonds. Both polymers consist of magnetically isolated $[\text{Mn}_6]$ SMMs with $S \approx 4$ ground states. We continue exploiting $[\text{Mn}_{3/6}]$ SMMs as starting materials for the construction of polymeric molecular magnetic materials with the next stage being to introduce added functionality through the presence of redox-active or radical linker ligands which might enable [stronger] communication between the cluster building blocks.

Notes and references

‡ Crystal data for **1**: $\text{C}_{224}\text{H}_{220}\text{Mn}_{24}\text{N}_{24}\text{O}_{101.50}$, $M = 6190.80$, triclinic, $a = 12.5838(4) \text{ \AA}$, $b = 19.5656(5) \text{ \AA}$, $c = 25.6050(6) \text{ \AA}$, $\alpha = 99.792(2)^\circ$, $\beta = 90.436(2)^\circ$, $\gamma = 97.756(2)^\circ$, $V = 6152.5(3) \text{ \AA}^3$, $T = 100(2) \text{ K}$, space group $P\bar{1}$, $Z = 1$, 121047 reflections measured, 24245 independent reflections ($R_{\text{int}} = 0.1296$). The final R_I values were 0.0674 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1494 ($I > 2\sigma(I)$). The final R_I values were 0.1601 (all data). The final $wR(F^2)$ values were 0.1759 (all data). Crystal data for **2**: $\text{C}_{83.70}\text{H}_{100.80}\text{Mn}_9\text{N}_9\text{O}_{42.20}$, $M = 2402.52$, triclinic, $a = 14.7534(4) \text{ \AA}$, $b = 16.3686(4) \text{ \AA}$, $c = 22.2983(6) \text{ \AA}$, $\alpha = 101.659(2)^\circ$, $\beta = 101.396(2)^\circ$, $\gamma = 96.649(2)^\circ$, $V = 5101.3(3) \text{ \AA}^3$, $T = 100 \text{ K}$, space group $P\bar{1}$, $Z = 2$, 42686 reflections measured, 19808 independent reflections ($R_{\text{int}} = 0.055$). The final R_I values were 0.0744 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0128 ($I > 2\sigma(I)$). The final R_I values were 0.1160 (all data). The final $wR(F^2)$ values were 0.0128 (all data).

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