Two-dimensional frameworks built from Single-Molecule Magnets

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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, π⋯π 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. To this end, we recently exploited certain members of a family of hexanuclear, [Mn₆], and trinuclear, [Mn₃], Mn³⁺ complexes of general formulae [Mn³⁺₆O₂(R-sao)₆(O₂CR)₂(L)₄] and [Mn³⁺₃O(R-sao)₃(X)(L)₃] (saoH₂ = salicylaldoxime; R = H, Me, Et etc; X = RCO₂⁻, ClO₄⁻; L = solvent) as building blocks for constructing discrete and infinite supramolecular architectures with the use of both bis-pyridyl and bis-carboxylate 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.

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] and the 2D coordination polymer [Mn₆O₂(sao)₆(tma)(MeOH)₃.₃₃(H₂O)₁.₃₃·(MeOH)₄.₄₆(H₂O)]·(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.

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 magnetometry\textsuperscript{7}, it is much more efficient to simply perform the reactions \textit{in situ}. The Mn(ClO\textsubscript{4})\textsubscript{2}·6H\textsubscript{2}O / saoH / tmaH\textsubscript{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\textsubscript{3} is added into an alcoholic solution containing Mn(ClO\textsubscript{4})\textsubscript{2}·6H\textsubscript{2}O / saoH / MeONa, while the 2D coordination polymer 2 is formed when MeONa was added into an alcoholic solution containing Mn(ClO\textsubscript{4})\textsubscript{2}·6H\textsubscript{2}O / saoH / tmaH\textsubscript{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 $P\overline{1}$.\textsuperscript{‡} The assymetric unit consists of two tmaH\textsubscript{2}\textsuperscript{−} anions, one [Mn\textsuperscript{III}\textsubscript{6}] and two [Mn\textsuperscript{III}\textsubscript{3}] units.\textsuperscript{†} In effect, there are two crystallographically independent [Mn\textsubscript{6}] clusters, namely [Mn\textsubscript{6}]\textsubscript{A} and [Mn\textsubscript{6}]\textsubscript{B}, repeating along the chain of 1. Each [Mn\textsubscript{6}] unit consists of two off-set, stacked [Mn\textsuperscript{III}\textsubscript{3}O(sao)\textsubscript{3}]\textsuperscript{+} triangles linked by two oximato O- atoms, while one phenolato O- atom bridges between the [Mn\textsubscript{3}] subunits in [Mn\textsubscript{6}]\textsubscript{A}. Four sao\textsubscript{2}\textsuperscript{−} ligands bridge along the edges of the [Mn\textsubscript{3}] subunits in a $\mu_{5}:\eta^{1}:\eta^{1}:\eta^{2}$ fashion, one in a $\mu_{5}:\eta^{2}:\eta^{3}:\eta^{1}$ fashion while the remaining seven sao\textsubscript{2}\textsuperscript{−} ligands adopt the $\mu_{5}:\eta^{1}:\eta^{1}:\eta^{3}$ coordination mode. Ten out of the twelve crystallographically independent Mn\textsuperscript{III} atoms are in an (axially) elongated octahedral environment with one Mn\textsuperscript{III} in each of the [Mn\textsubscript{6}] clusters being five-coordinate and in a square pyramidal environment. Nine MeOH molecules (one is 50\% disordered with a H\textsubscript{2}O molecule) occupy the Jahn Teller positions on the Mn\textsuperscript{III} ions, with the remaining sites coordinated by carboxylato O- atoms from the two crystallographically independent tmaH\textsubscript{2}\textsuperscript{−} ligands. These ligands adopt the $\mu_{5}:\eta^{1}:\eta^{1}:\eta^{1}$ and $\mu_{5}:\eta^{1}:\eta^{1}:\eta^{1}$ coordination modes, respectively. The Mn-N-O-Mn torsion angles for [Mn\textsubscript{6}]\textsubscript{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 [Mn\textsubscript{6}]\textsubscript{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.
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 [Mn\(_6\)]\(_B\) clusters serve as 3- and 4-connected nodes within the 2D network, respectively, with [Mn\(_6\)]\(_A\) simply bridging between the tmaH\(^2\)-ligands.

Complex 2 also crystallises in the triclinic space group \(P\bar{T}\).‡ The asymmetric unit consists of one tma\(^3\)-anion and three [Mn\(^{III}\)O(sao)\(_3\)]\(^+\) subunits (Fig. 2).† This arrangement gives rise to three crystallographically independent [Mn\(_3\)] clusters, with each sitting on an inversion centre. Two off-set stacked [Mn\(^{III}\)O(sao)\(_3\)]\(^+\) triangles linked by two oximato O-atoms create each [Mn\(_3\)] cluster. Therefore, four sao\(^2\)-ligands bridge along the edges of the [Mn\(_3\)] subunits in a \(\mu_2\eta^1\cdot\eta^1\) fashion, while two sao\(^2\)-ligands adopt the \(\mu_3\eta^1\cdot\eta^1\cdot\eta^2\) coordination mode. Two Mn\(^{III}\) ions in each [Mn\(_3\)] 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\(_2\)O 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$^{\text{III}}$ ions. The tma$^{3-}$ ligand bridges five Mn$^{\text{III}}$ ions, from three different [Mn$_6$] clusters, adopting the $\mu_5:\eta^1:\eta^1:\eta^1:\eta^1$ 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 [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 [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 [Mn$_6$].

The [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 [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 [Mn$^{III}_6$] and [Mn$^{III}_3$] 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 [Mn$_n$] 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 $\chi_M T$ versus $T$ for 1 and 2 are shown in Fig. S1. The $\chi_M T$ products at 275 K are 16.54 and 14.95 cm$^3$ mol$^{-1}$ K for 1 and 2, respectively, close to the spin-only ($g = 2$) value of 18 cm$^3$ mol$^{-1}$ K expected for a [Mn$_n$] unit comprising six high spin Mn$^{III}$ ions. The $\chi_M T$ values for both complexes remain approximately constant as the temperature is lowered, before dropping more rapidly at temperatures below 125 K. Thereafter, the $\chi_M T$ value for complex 1 decreases constantly to reach a value of 9.1 cm$^3$ mol$^{-1}$ K at 5 K, while that for complex 2 decreases to a value of ~8.0 cm$^3$ mol$^{-1}$ K at 20 K and then plateaus to 5 K. The decrease of the $\chi_M T$ 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 [Mn$^{III}_6$] units in both complexes. Indeed we note that the $\chi_M T$ behaviour for 1 and 2 is very similar to that observed for previously reported and magnetically isolated [Mn$^{III}_6$] complexes with $S = 4$ spin ground states. For comparison we include in Figure S1 the data for [Mn$_n$O$_2$(sao)$_n$(ketoacetate)$_2$(EtOH)$_2$(H$_2$O)$_2$] (3) and [Mn$_n$O$_2$(sao)$_n$(1-Me-cyclohexit)$_2$(MeOH)$_4$] (4) from reference 3c which contain [Mn$_n$] 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 $\chi'$ (Fig. S3) is accompanied by a non-zero imaginary component $\chi''$ 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 $\chi''$ data afford $r_0 = 3.3 \times 10^{-9}$ s and $U_{\text{eff}} = 32.84$ K (22.82 cm$^{-1}$) for 1, and $r_0 = 5.6 \times 10^{-6}$ s and $U_{\text{eff}} = 24.54$ K (17.05 cm$^{-1}$) for 2. The presence of significant inter-[Mn$_n$] 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 $k = \Delta T_B/(T_B \Delta \log f)$, where $\Delta T_B$ is the change in $T_B$ for the given change in frequency $\Delta \log f$, were $\Delta \log f = 1.30$ 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 [Mn$_n$] 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 $\chi''$ versus $T$ for complex 1 at the indicated temperature and frequency ranges. Inset: Arrhenius plot constructed from the $\chi''$ 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 $[\text{Mn}_n]$ 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 $[\text{Mn}_n]$ 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: C_{224}H_{220}Mn_{24}N_{24}O_{101.50}, M = 6190.80, triclinic, a = 12.5838(4) Å, b = 19.5656(5) Å, c = 25.6050(6) Å, α = 99.792(2)°, β = 90.436(2)°, γ = 97.756(2)°, V = 6152.5(3) Å³, T = 100(2) K, space group P1̅, Z = 1, 121047 reflections measured, 24245 independent reflections (R_{int} = 0.1296).

The final R values were 0.0674 (I > 2σ(I)). The final wR(F²) values were 0.1494 (I > 2σ(I)). The final R values were 0.1601 (all data). The final wR(F²) values were 0.1759 (all data).

Crystal data for 2: C_{83.70}H_{100.80}Mn_{9}N_{9}O_{42.20}, M = 2402.52, triclinic, a = 14.7534(4) Å, b = 16.3686(4) Å, c = 22.2983(6) Å, α = 101.659(2)°, β = 101.396(2)°, γ = 96.649(2)°, V = 5101.3(3) Å³, T = 100 K, space group P1̅, Z = 2, 42686 reflections measured, 19808 independent reflections (R_{int} = 0.055). The final R values were 0.0744 (I > 2σ(I)). The final wR(F²) values were 0.0128 (I > 2σ(I)). The final R values were 0.1160 (all data). The final wR(F²) values were 0.0128 (all data).


