

Dimeric and Tetrameric Supramolecular Aggregates of Single-Molecule Magnets via Carboxylate Substitution

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Supporting Information

ABSTRACT: $[\text{Mn}_3]_2$ and $[\text{Mn}_3]_4$ supramolecular aggregates of weakly exchange-coupled Mn^{III} single-molecule magnets (SMMs) with $S = 6$ have been prepared by carboxylate substitution on $[\text{Mn}_3\text{O}(\text{O}_2\text{CMe})_3(\text{mpko})_3]^+$ [mpkoH = methyl(pyridine-2-yl) ketone oxime] with the dicarboxylic acids α -truxillic acid and fumaric acid, respectively. The method opens up a new approach to Mn_3 SMM aggregates of various size and topology.

Single-molecule magnets (SMMs) are molecules that function as single-domain nanoscale magnetic particles below their blocking temperature, T_B .^{1,2} For 3d transition-metal clusters, this behavior arises from the combination of a large ground-state spin (S) and Ising-type magnetoanisotropy (negative zero-field-splitting parameter, D), which leads to frequency-dependent out-of-phase alternating-current (ac) magnetic susceptibility signals, and hysteresis in a plot of magnetization versus applied direct-current (dc) magnetic field.¹ They also display quantum phenomena such as quantum tunneling of magnetization (QTM)³ and quantum phase interference⁴ and have been proposed as qubits for quantum computation⁵ and as components in molecular spintronics.⁶ Molecules functioning as nanoscale magnets bring the advantages of molecular chemistry to the area, such as solubility in common solvents and crystals of monodisperse units identically oriented. It often also allows the organic ligands to be modified using standard ligand substitution methods, and the latter have been crucial in allowing targeted modification of SMMs such as the Mn_4 and Mn_{12} families,⁷ with a profound impact on many studies, including those probing their quantum properties.

For applications of SMMs in new technologies, the quantum mechanical coupling of two or more to each other or to other components of a device, while maintaining the intrinsic single-molecule properties of each SMM, is essential. Such couplings were established in hydrogen-bonded SMM dimers and were manifested as exchange-biased QTM, quantum superposition states, and quantum entanglement.^{8,9} We have since extended this work to covalently linked SMM oligomers to provide greater synthetic control; such covalent linkage of preformed SMMs has been extensively studied previously and usually, but not always, leads to 1D, 2D, or 3D polymers.¹⁰ We reported a rectangular $[\text{Mn}_3]_4$ tetramer of $S = 6$ Mn_3 SMMs¹¹ by using a dioxime instead of the monooxime mpkoH [methyl(pyridine-2-yl) ketone oxime] in the preparation of $[\text{Mn}_3\text{O}(\text{O}_2\text{CMe})_3(\text{mpko})_3](\text{ClO}_4)$ (**1**; Figure 1).¹² We are continuing work with dioximes and also

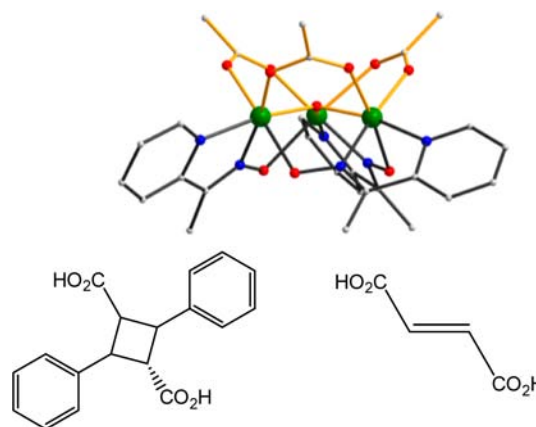


Figure 1. Structures of the cation of **1** (top), α -truxillic acid (bottom left), and fumaric acid (bottom right). Color code: Mn, green; N, blue; O, red; C, gray.

investigating aggregation of **1** at the carboxylate sites using dicarboxylates. The cation of **1** was attractive because the tripodal arrangement of its acetates could favor discrete aggregates. Such carboxylate substitution reactions are with precedent in manganese chemistry, e.g., with clusters such as $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$.² We herein report some initial results of this work, tetrameric $[\text{Mn}_3]_4$ and dimeric $[\text{Mn}_3]_2$ aggregates from the use of fumaric acid (fumH_2) and α -truxillic acid (atxH_2), respectively (Figure 1).

The reaction of **1** and fumH_2 in a 4:6 ratio in MeCN gave a dark-brown solution. Toluene was added and the solvent removed in vacuo, and five more cycles of dissolution in MeCN, addition of toluene, and solvent removal were carried out to remove all acetic acid as its toluene azeotrope. The residue was dissolved in MeCN and layered with toluene, and brown-black crystals of $[\text{Mn}_{12}\text{O}_4(\text{fum})_6(\text{mpko})_{12}](\text{ClO}_4)_4$ (**2**) slowly grew in 35% yield as $2 \cdot x\text{C}_7\text{H}_8 \cdot y\text{MeCN}$. These were collected by filtration and washed with toluene and Et_2O .¹³ The reaction of **1** and bulky atxH_2 in a 4:6 ratio in MeCN/EtOH (2:1, v/v) gave a dark-brown solution. After three cycles of toluene addition and solvent removal, the residue was dissolved in MeCN/EtOH and layered with Me_2CO /hexane. $[\text{Mn}_6\text{O}_2(\text{atx})_4(\text{mpko})_6]$ (**3**) slowly crystallized in 30% yield as $3 \cdot x\text{Me}_2\text{CO} \cdot y\text{MeCN}$ and was collected by filtration, washed with Et_2O , and dried under vacuum.¹³

The cation of **2** (Figure 2) comprises an $[\text{Mn}_3]_4$ tetrahedron with a fum^{2-} bridging each edge to give an adamantane-like

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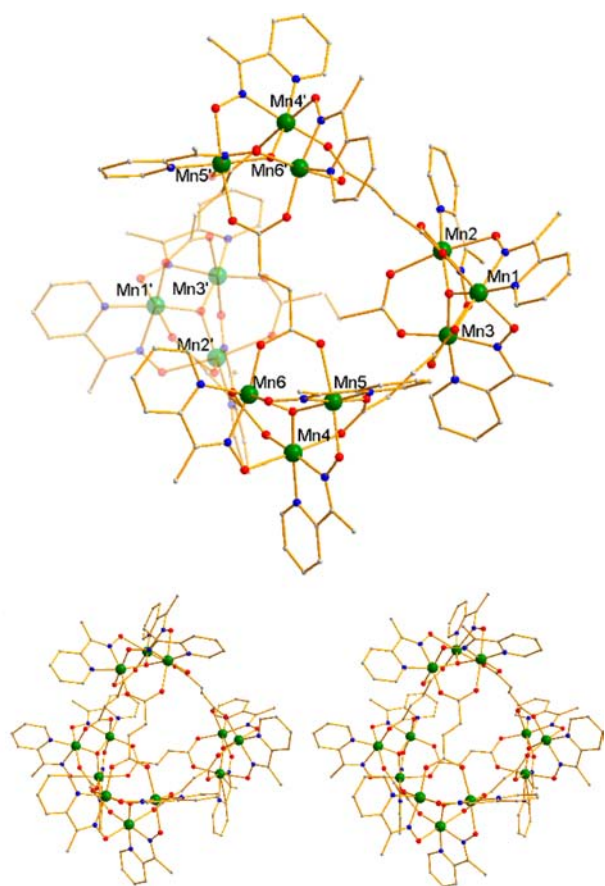


Figure 2. Complete structures of **2** (top) and a stereopair (bottom). H atoms are omitted for clarity. Color code: Mn, green; N, blue; O, red; C, gray.

structure, a common unit in supramolecular chemistry.¹⁴ Each fum^{2-} carboxylate group is $\eta^1:\eta^1:\mu$ and thus bridges within a Mn_3 unit like the acetate that it replaced. In fact, the local structure of each Mn_3 is very similar to that in **1**, and thus **2** can accurately be described as a tetramer of **1** held together by fum^{2-} linkers. There is a disordered toluene guest molecule in the central cavity of **2**. Examination of space-filling figures clearly suggested that atxH_2 could not form the same type of $[\text{Mn}_3]_4$ tetrahedron because of the 12 bulky Ph substituents to be accommodated, and it was of interest to see if it would instead yield a rectangular topology, as we had previously seen for the dioximate-bridged $[\text{Mn}_3]_4$ or something else. In fact, **3** is a $[\text{Mn}_3]_2$ dimer (Figure 3) but is additionally interesting in that for clear steric reasons it is bridged by only two atx^{2-} groups (Figure 3, bottom), with two additional atx^{2-} binding only through one carboxylate at each Mn_3 .

The structures of **2** and **3** indicate that the Mn_3 unit of **1** has been aggregated without changing its Mn^{III} oxidation level,¹³ the triangular topology, or the propeller-like disposition of its mpko^- groups and Mn^{III} Jahn–Teller axes (Figures 2 and 3) and with only minor changes to metric parameters. We thus anticipated that each Mn_3 unit would still be ferromagnetically coupled with an $S = 6$ ground state but with weak inter- Mn_3 interactions through the dicarboxylates.

Variable-temperature magnetic susceptibility (χ_M) studies were performed on vacuum-dried microcrystalline samples, restrained in eicosane to prevent torquing, in a 1000 G (0.10 T) dc field, and in the 5.0–300 K temperature range. The data are shown as $\chi_M T$ versus T in Figure 4, and the increasing $\chi_M T$ with

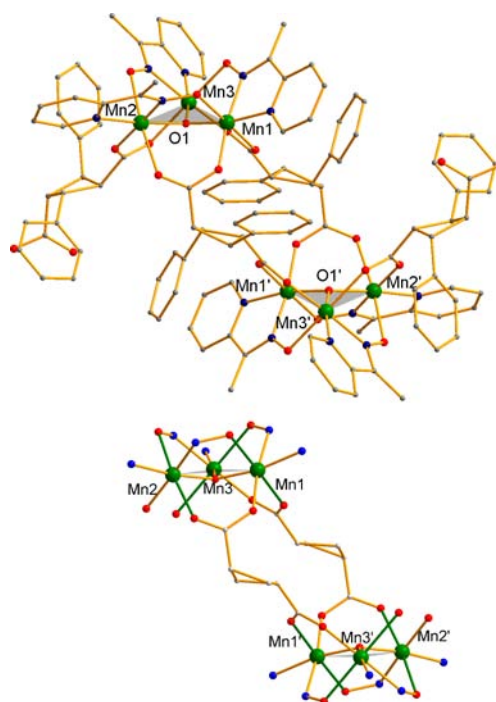


Figure 3. Structures of **3** (top) and its core (bottom), with the Jahn–Teller axes shown in green. H atoms are omitted for clarity. Color code: Mn, green; N, blue; O, red; C, gray.

decreasing T is as seen for **1** and indicates that the exchange interactions within each Mn_3 are still ferromagnetic. For **3**, $\chi_M T$ increases from $23.56 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K to a plateau value of $38.57 \text{ cm}^3 \text{ K mol}^{-1}$ at 20 K before decreasing slightly to $35.31 \text{ cm}^3 \text{ K mol}^{-1}$ at 5.0 K. The plateau value is as expected for two “noninteracting” $S = 6$ units with $g \sim 1.92$, with the spin-only ($g = 2.0$) $\chi_M T$ being $42 \text{ cm}^3 \text{ K mol}^{-1}$. Thus, any interactions between the two Mn_3 are too weak to show up at $T > 20$ K, as expected. Similarly, the plateau value for **2** of $\sim 73 \text{ cm}^3 \text{ K mol}^{-1}$ is lower than the spin-only value of $84 \text{ cm}^3 \text{ K mol}^{-1}$ for four noninteracting $S = 6$ Mn_3 units. The decreases at $T < 20$ K are assigned primarily to zero-field-splitting and Zeeman effects of the applied field. The data for **2** and **3** were fit to the theoretical $\chi_M T$ versus T expression for four and two independent Mn_3^{III} isosceles triangles, respectively, as described for **1**;¹² the spin Hamiltonian is given in eq 1.

$$\mathcal{H} = -2J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_1 \cdot \hat{S}_2) - 2J' \hat{S}_2 \cdot \hat{S}_2 \quad (1)$$

The fits (solid lines in Figure 4), which excluded the low- T data, gave $J = +5.5(1) \text{ cm}^{-1}$, $J' = +23.4(4) \text{ cm}^{-1}$, and $g = 1.89(2)$ for **2** and $J = +14.4(7) \text{ cm}^{-1}$, $J' = +4.6(9) \text{ cm}^{-1}$, and $g = 1.91(2)$ for **3**, with a constant TIP of $300 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ per Mn_3 included for both complexes. These values are comparable with those for **1** and related monomers ($J = +12.1$ to $+18.6 \text{ cm}^{-1}$ and $J' = +1.5$ to $+6.7 \text{ cm}^{-1}$, depending on the carboxylate).¹²

Finally, ac susceptibility studies of **2** and **3** in a 3.5 G ac field and in the 1.8–15 K range gave near-plateau values of the in-phase $\chi'_M T$ of ~ 73 and $\sim 39 \text{ cm}^3 \text{ K mol}^{-1}$, respectively, in the 10–15 K range, showing that the plateau values in the dc plot (Figure 4) are not artifacts of the applied field. At temperatures below 3 K, there are frequency-dependent drops in the $\chi'_M T$ versus T plots and the concomitant appearance of out-of-phase (χ''_M) signals (Figure 3, insets), indicating the slow relaxation of SMMs. This is again similar to **1** and indicates the Mn_3 units

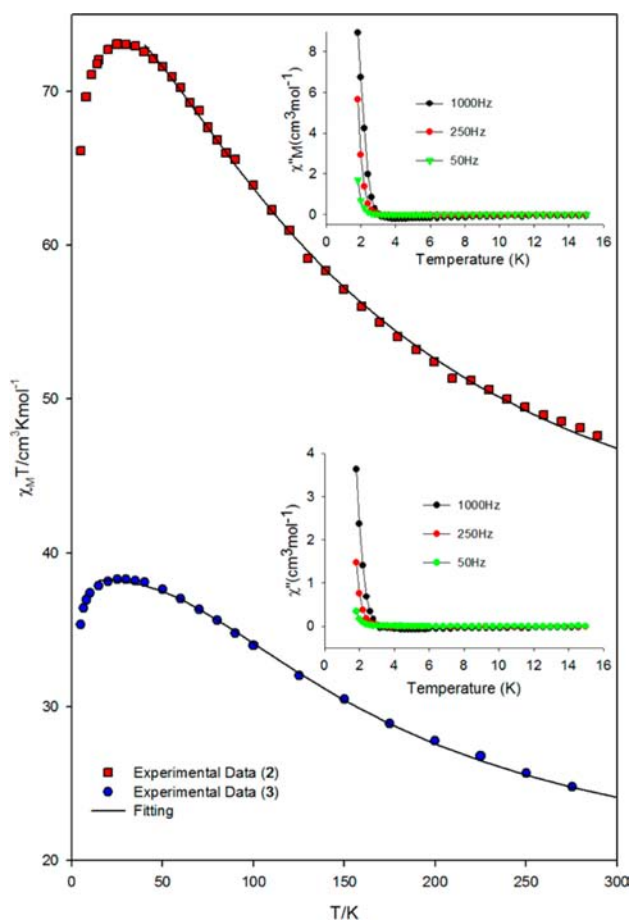


Figure 4. $\chi_M T$ versus T (per mole of aggregate) for complexes **2** and **3**. The solid lines are fits to the data; see the text for the fit parameters. Insets: Out-of-phase (χ''_M) ac susceptibility versus T at the indicated frequencies for **2** (upper inset) and **3** (lower inset).

within the tetramer and dimer aggregates are only weakly interacting and retain the intrinsic SMM properties of the monomeric Mn_3 .

In conclusion, **2** and **3** establish that supramolecular aggregates of the Mn_3 SMMs may be attained through the carboxylate sites of **1**, complementing our previous report of aggregation at the oximate position using dioximates.¹¹ The latter route is not by substitution on preformed **1** but by direct synthesis; nevertheless, we now have the option of site-selectively aggregating at the carboxylate or oxime positions or indeed sequentially at both. This and the many dicarboxylic acids and dioximes with a variety of lengths, shape, and bulk that are available commercially or easily synthesized promise access to various oligomers of SMMs with differing topologies and strengths of inter- Mn_3 interactions. The fact that the Mn_3 planes in **3** are parallel provides an optimal situation for the study of their quantum mechanical coupling, and higher oligomers with such a feature are under investigation, as are a variety of other systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic details in CIF format, bond distances and angles, and ac magnetism data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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