Enhancing SMM properties *via* axial distortion of Mn^{III}_3 clusters†

Ross Inglis,[a] Leigh F. Jones,[a] Georgios Karotsis,[a] Anna Collins,[a] Simon Parsons,[a]
Spyros P. Perlepes,[b] Wolfgang Wernsdorfer*[c] and Euan K. Brechin*[a]

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Replacement of carboxylate and solvent with facially capping tripodal ligands enhances the single-molecule magnet (SMM) properties of $[Mn^{III}_3]$ triangles.

Studies of the magnetic behaviour of molecular cluster compounds have seen a resurgence in recent years because such species are the gateway for discovering fascinating new physics.[1–13] The emergence of *molecular nanomagnets*[14] in proposed applications as diverse as information storage, molecular spintronics, quantum computation, magnetic refrigeration and MRI has seen synthetic chemists, physicists, theoreticians and materials scientists working in tandem to create, understand and design molecules with specific properties.

Single-molecule magnets[15] and magnetic refrigerants[16] require molecules to possess large spin ground states. This is a non-trivial target, especially as the nuclearity of the molecule increases. The most commonly employed, and successful, technique involves combining metal ions with large numbers of unpaired electrons with flexible bridging ligands to form polymetallic clusters whose identity is not pre-known.[15] An alternative strategy which is rapidly growing in popularity is the targeted structural distortion of known molecules—the idea being that even small changes in geometry can have a major impact on exchange interactions. This is a strategy which has seen some striking recent success.[17]

The discovery of the unusual ferromagnetic exchange in the clusters $[Mn_3O(bamen)_3]^+$ and $[Mn_3O(mpko)_3(O_2CR)_3]^+$,[18] simple analogues of the (antiferromagnetic) basic carboxylates $[M_3O(O_2CR)_6L_3]^{0,+}$, stimulated us to examine whether the weak exchange propagated through oxime (Mn–N–O–Mn) bridges could be switched from antiferromagnetic (AF) to ferromagnetic (F) and *vice versa via* targeted structural distortion. This proved successful in clusters of derivatised phenolic oximes (R-saoH$_2$) of general formula $[Mn^{III}_6O_2(R\text{-sao})_6(O_2CR')_2L_{4-6}]$ where increased bulk in the R-group resulted in increased puckering or "twisting" of the magnetic core of the molecule resulting in the stabilisation of the ferromagnetic $S = 12$ ground state; the switch from AF → F seemingly related to the Mn–N–O–Mn torsion angles.[17d,e,19] In all of the hexametallic and analogous trimetallic $[Mn^{III}_3O(R\text{-sao})_3(O_2CR')L_4]$ (L = py, ROH) cluster compounds[17d,20] we have reported, the structural distortion derives from the replacement of a "planar" equatorial oxime ligand (R-saoH$_2$; R = H) with a "non-planar" equatorial oxime ligand (R-saoH$_2$; R = Me, Et, Ph). Herein we show that it is also possible to replace the axial carboxylate and solvent ligands with face capping tripodal ligands maintaining the structural integrity of the magnetic core but increasing its distortion and greatly enhancing its SMM properties.

The molecular structures of $[Mn^{III}_3O(Et\text{-sao})_3(ReO_4)(EtOH)(H_2O)_2]\cdot 3EtOH$ (**1**·3EtOH) and $[Mn^{III}_3O(Et\text{-sao})_3(ClO_4)(MeOH)_3]$ (**2**)†‡ are shown in Fig. 1. Complex **1** crystallises in the triclinic space group $P\bar{1}$ and **2** in the trigonal space group $R\bar{3}$. Their structures are analogous, comprising an oxo-centered [Mn(III)$_3$] triangle in which the three μ-Et-sao^{2-} ligands span each edge of the triangle using their –N–O– oxime moiety to bridge between adjacent Mn(III) ions; their phenolic O-atoms being terminally bound. The "lower" face of the Mn$_3$ triangle is occupied by three solvent (EtOH, MeOH, H$_2$O) molecules and the "upper" face by the sole tripodal ligand: ReO_4^- in **1** and ClO_4^- in **2**. To the best of our knowledge this is the first time the perrhenate anion has been employed as an inorganic tripodal ligand in 3d cluster chemistry. The Jahn–Teller axes are perpendicular to the Mn$_3$ plane with Mn–O bond lengths in the range ∼2.15–2.29 Å (solvent) and ∼2.38–2.55 Å (XO_4^-). Both molecules are clearly very puckered with the R-sao^{2-} ligands significantly out of the Mn$_3$ plane, as reflected in Mn–N–O–Mn torsion angles of ∼40.2, 41.8, 43.7° for **1** and ∼42.1° for **2**. The O^{2-} ion is co-planar with the Mn ions in **1** (∼0.04 Å) but shifted out of the plane in **2** (∼0.18 Å). There are significant intermolecular interactions in both, propagated by the O-atoms of the lower face alcohols/H$_2$O: in **2** these are directly H-bonded to phenolic O-atoms on neighbouring molecules (there are no solvent molecules in the lattice) whereas in **1** they are propagated through "intermediary" EtOH solvent molecules (O···O, ∼2.6–2.8 Å). In each case the result is that nearest neighbours are packed in a head-to-tail fashion throughout the crystal and for **2** this affords an aesthetically pleasing honeycomb-like topology (Fig. 1).

The parent members of this family $[Mn^{III}_3O(R\text{-sao})_3(O_2CR')(py)_4]$ are all characterised by antiferromagnetic exchange between the metal centres and $S = 2$ spin ground states.[20] According to our previous magneto-structural correlations on the analogous $[Mn^{III}_6]$ complexes, Mn–O–N–Mn torsion angles above approximately 31° should give rise to

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[a] *School of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ*
E-mail: ebrechin@staffmail.ed.ac.uk; Tel: +44 0131-650-7545
[b] *Department of Chemistry, University of Patras, 26504 Patras, Greece*
[c] *Institut Néel, CNRS & Université J. Fourier, BP 166, 38042 Grenoble, France. E-mail: wolfgang.wernsdorfer@grenoble.cnrs.fr*

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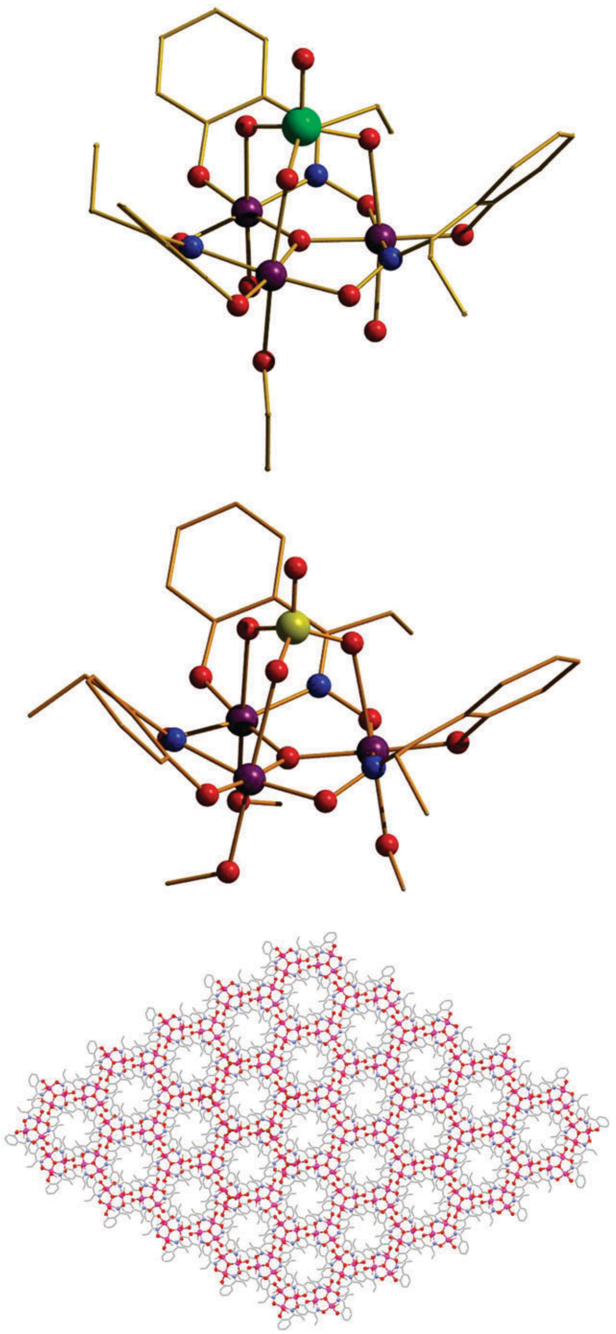

Fig. 1 The molecular structures of **1** (top) and **2** (middle); and the packing of **2** in the crystal viewed down the *c*-axis (bottom). Mn = purple; O = red; N = blue, Re = green; Cl = yellow.

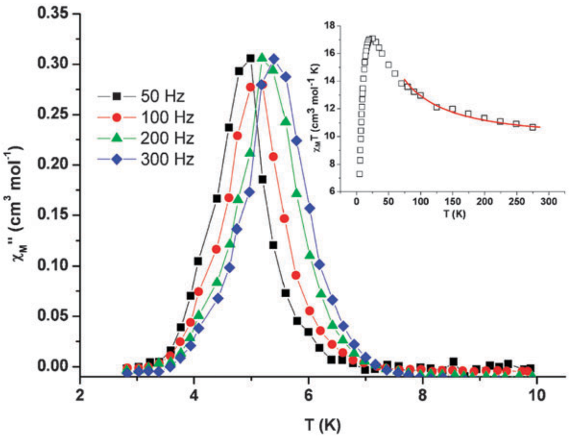

Fig. 2 Plot of the out-of-phase (χ_M'') ac susceptibility *versus* temperature for **2** in the indicated frequency ranges. The inset shows the dc susceptibility; the solid line is a fit of the experimental data. See text for details.

ferromagnetic exchange.[17d,e] Because the magnetic behaviour of **1** and **2** are rather similar and for the sake of brevity we will limit our discussion herein to complex **2**. Dc susceptibility measurements were carried out in the 300–5 K temperature range in an applied field of 0.1 T. The room temperature $\chi_M T$ value of $\sim$10 cm^3 K mol^{-1} is larger than the spin-only value expected for an uncoupled [Mn$^{III}{}_3$] unit of 9 cm^3 K mol^{-1} (Fig. 2). The value then increases with decreasing temperature reaching a maximum of $\sim$17 cm^3 K mol^{-1} at $\sim$20 K. The drop in $\chi_M T$ below this temperature is assigned primarily to the significant intermolecular antiferromagnetic interactions (and/or zero-field splitting (ZFS) effects). The behaviour is clearly indicative of intra-molecular ferromagnetic exchange. A fit of the experimental data using the 1*J* model (the complex has three-fold symmetry) of eqn (1) affords the parameters $S = 6$, $g = 2.0$ and $J = +2.8$ cm^{-1}.[21] The fit is good down to $\sim$75 K below which the experimental curve decreases in magnitude never reaching the value of 21 cm^3 K mol^{-1} expected for $S = 6$, consistent with the significant inter-molecular interactions in the crystal. A plot of χ_M *versus* *T* in combination with the in-phase (χ_M' plotted as $\chi_M'T$ *versus* *T* in Fig. S1 and S2†) ac susceptibility is also in agreement with the presence of inter-molecular interactions.

$$\hat{\mathscr{H}} = -2J[(\hat{S}_1 \cdot \hat{S}_2) + (\hat{S}_2 \cdot \hat{S}_3) + (\hat{S}_1 \cdot \hat{S}_3)] \qquad (1)$$

In order to confirm the spin ground state and determine $|D|$, magnetisation data were collected in the ranges 0.5–7.0 T and 2–7 K. These are plotted as reduced magnetisation ($M/N\mu_B$) *vs.* H/T in Fig. S3.† The data saturate at $M/N\mu_B \approx 10.5$ indicative of an $S = 6$ state with significant $|D|$. Attempts to fit the experimental data with an axial ZFS plus Zeeman Hamiltonian, eqn (2),[22] over the whole field and temperature range failed. The best fits, although still rather poor, came from employing only the high field, low temperature data affording $S = 6$ with $D \approx -0.95$ cm^{-1}.

$$\mathscr{H} = D(\hat{S}_z{}^2 - S(S + 1)/3) + \mu_B g H \hat{S} \qquad (2)$$

Ac susceptibility studies carried out on crystalline samples of **2** in the 1.8–10.0 K range in a 3.5 G field oscillating at frequencies up to 300 Hz display frequency-dependent out-of-phase (χ_M'') signals suggestive of SMM behaviour with the 300 Hz peak appearing at a temperature of $\sim$5 K (Fig. 2). In combination with single crystal dc relaxation measurements, these data were then used to construct an Arrhenius plot (Fig. S4†) from which fitting of the Arrhenius equation gave $U_{eff} = 57.8$ K and $\tau_0 = 1.88 \times 10^{-9}$ s. This is the largest effective barrier observed for any low nuclearity ($n < 6$) SMM. Hysteresis loop and relaxation measurements were carried out on single crystals of **2** using a micro-SQUID assembly, with the field applied along the easy axis of magnetisation.[23]

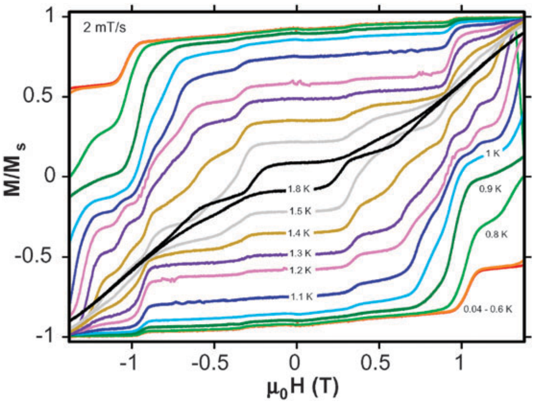

Fig. 3 Magnetisation *versus* field hysteresis loops for a single crystal of **2** at the indicated temperatures and field sweep rate. *M* is normalised to its saturation value.

Temperature and sweep rate dependent hysteresis loops were observed confirming SMM behaviour (Fig. 3). The loops display step-like features separated by plateaus. After saturating the magnetisation, the first resonance is seen in negative fields, indicative of the presence of intermolecular antiferromagnetic interactions. A detailed study of the hysteresis loops show that the collective spins of each [Mn_3] molecule are coupled antiferromagnetically to its neighbouring molecules, acting as a bias that shifts the quantum tunnelling resonances with respect to the isolated SMM.[4] Most of the small steps are therefore due to molecules having one or several reversed neighbouring molecules, although some of the steps may also be due to multi-body quantum effects and to the presence of excited state multiplets.[24] Indeed, the exchange bias is so complicated that it is difficult to identify the exchange coupling strength or the magnitude of $|D|$. In order to do this we must first synthesise the analogous molecules but in the absence of intermolecular interactions, *i.e.* replace the terminally bound solvent molecules. These studies are currently in progress.

Notes and references

‡ The complex analysed as **1**·EtOH. Elemental analysis, expected (found): C, 35.50 (35.41); H, 4.13 (4.42); N, 4.01 (4.31)%. Diffraction data were collected with Mo-Kα radiation (λ = 0.71073 Å) on a Bruker Smart Apex CCD diffractometer. Crystal data: $C_{35}H_{45}N_3O_{17}ReMn_3$, M = 1140.82, black block, triclinic, $P\bar{1}$, a = 13.2285(7), b = 13.7060(7), c = 15.0998(8) Å, α = 85.868(3), β = 65.017(2), γ = 62.085(2)°, V = 2165.7 Å^3, Z = 2, T = 150 K, 29 075 reflections collected of which 8837 were independent (R_{int} = 0.049), 532 parameters and 13 restraints, $R1$ = 0.0360 [based on $F > 4\sigma(F)$], $wR2$ = 0.0875 (based on F^2 and all data). CCDC 694668. The complex analysed as **2**. Elemental analysis, expected (found): C, 41.61 (41.32); H, 4.54 (4.76); N, 4.81 (5.03)%. Diffraction data were collected with Mo-Kα radiation (λ = 0.71073 Å) on a Bruker Smart Apex CCD diffractometer. Crystal data: $C_{30}H_{39}N_3O_{14}ClMn_3$, M = 865.89, black square, trigonal, $R\bar{3}$, a = 13.3784(3), b = 13.3784(3), c = 34.0617(12) Å, α = 90.0, β = 90.0, γ = 120.0°, V = 5279.7(3) Å^3, Z = 6, T = 150 K, 63 184 reflections collected of which 3607 were independent (R_{int} = 0.036), 154 parameters and 0 restraints, $R1$ = 0.0288 [based on $F > 4\sigma(F)$], $wR2$ = 0.0679 (based on F^2 and all data). CCDC 694669.

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