A Single-Molecule Magnet with a “Twist”

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The origin of the ferromagnetic exchange in a recently reported oxo-centered triangular Mn(III) single-molecule magnet (SMM) based on oximato ligands is fascinating since the exchange in all other complexes containing the \([\text{Mn}^{III} \cdot \text{O}]^{7}\) core, including the well-known “basic carboxylates” of general formula \([\text{Mn}^{III} \cdot \text{O}(\text{O}_2 \cdot \text{CR})_2 \text{L}_3]^+(R = \text{Me, Et; L = py, MeCN, etc.})\), is antiferromagnetic.¹

We speculate that a structural distortion in the core of the molecule caused primarily by the “twisting” of the oximato ligands (with regard to the Mn³ plane) is responsible. In order to test this hypothesis we have made a family of novel ligands based on salicylaldoxime (saoH₂) in which the oximate carbon atom has been derivatized to possess the “bulky” Me (Me-saoH₂), Et (Et-saoH₂), and Ph (Ph-saoH₂) groups, and synthesized analogues of the known hexanuclear SMM \([\text{Mn}^{III} \cdot \text{O}(\text{sao})_2(\text{O}_2 \cdot \text{CPh})_2(\text{EtOH})_4]^2\) (1).² Complex \(1\), obtained upon the reaction of \(\text{Mn}(\text{O}_2 \cdot \text{CPh})_2 \cdot 2\text{H}_2\text{O}\) with saoH₂ in EtOH (Figure S1) contains a nonplanar \([\text{Mn}^{III}_6(\mu_3-\text{O})(\mu_3-\text{O})]^{12+}\) unit of two off-set, stacked \([\text{Mn}^{III}_2(\mu_3-\text{O})]^{12+}\) triangular subunits linked by two central oximato oxygens, with the remaining four sao²⁻ ligands bridging in a near-planar \(\eta^1: \eta^1: \eta^1: \mu^1\) fashion along the edges of the \([\text{Mn}^{III}_6(\mu_3-\text{O})]^{12+}\) triangles. The four “central” metals (Mn1, Mn3) are six-coordinate and in distorted octahedral geometries, while the outermost Mn ions (Mn2) have square pyramidal geometries with an additional axial contact of ~3.5 Å to a phenolato oxygen. The coordination geometry of the metal ions is completed by a combination of terminal alcohols and \(\mu\)-carboxylate groups. ¹ displays an \(S = 4\) spin ground state as a result of ferromagnetic exchange between the two antiferromagnetically coupled \(\text{Mn}^{III}\) triangles.²

The idea was to investigate whether the additional steric bulk of the derivatized oximates would enforce structural distortions similar to those seen in the ferromagnetic Mn³ triangle³ and the recently obtained ferromagnetic \([\text{Mn}^{III}_6(\text{Me-sao})_2(\text{Me-saoH})_2]^{2+}\) “cube”,² and thus switch the magnetic behavior from antiferromagnetic to ferromagnetic. Complex \([\text{Mn}^{III}_6(\text{Et-sao})_2(\text{O}_2 \cdot \text{CPh})_2(\text{EtOH})_4(\text{H}_2\text{O})_2]^2\text{EtOH}(2\cdot 2\text{EtOH})\) which contains the ethyl-derivatized saoH₂ (Et-saoH₂) does indeed display ferromagnetic exchange (\(S = 12\) ground state). Here we discuss its structure and magnetic properties. Complex 2 also crystallizes in the triclinic space group \(P\bar{1}\) and its structure (Figure 1) is analogous to that of 1.⁴ However, the increased steric bulk of the Et-sao²⁻ ligands causes a shortening of the phenolato oxygen (O71)–square pyramidal Mn (Mn3) distance (~2.5 Å) and severe twisting of the Mn–N–O–Mn moieties within each Mn₃ subunit (Figure 1). This is evidenced by the average Mn–N–O–Mn torsion angle, which in 1 is \(\alpha_r = 17.5^\circ\) compared to \(\alpha_r = 36.5^\circ\) for 2. This also results in a change in the coordination of the carboxylates: from \(\mu\)-bridging to terminal, with the “vacant” site now occupied by an additional solvent (alcohol) molecule.

Variable-temperature dc magnetic susceptibility data were collected on 2 in the temperature range 5–300 K in an applied field of 0.1 T (Figure S2). The room temperature \(\chi_M T\) value of 19.24 cm³ K mol⁻¹ is slightly above that expected for six noninteracting Mn³ ions (18 cm³ K mol⁻¹). Upon cooling the value of \(\chi_M T\) increases gradually to 23.72 cm³ K mol⁻¹ at ~70 K, below which it increases rapidly to a maximum value of 69.57 cm³ K mol⁻¹ at 6.5 K, before decreasing slightly to 69.36 cm³ K mol⁻¹ at 5 K. This behavior is indicative of ferromagnetic exchange between the metal centers with the low-temperature maximum suggesting an \(S = 12\) ground state. In order to confirm the ground state of the molecule, magnetization data were collected in the ranges 0.5–7 T and 1.8–7 K, and these are plotted as reduced magnetization (\(\Delta\bar{M}/\Delta\bar{M}_{50}\)) and the Zeeman interaction, and carries out a full powder average. The corresponding Hamiltonian is given by eq 1, ¹

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of the in-phase ($\chi''$) signal to 0 K from the plateau region gives a value of $6 \pm 1$ K with the peak at 1000 Hz occurring at $4.5 \pm 0.5$ K (Figure 4) using a micro-SQUID setup. 5 Hysteresis loops were targeted distortions to the core structures of Mn$_6$ (and other) clusters of SMMs to record values. May prove to be a viable means to raise the blocking temperatures of SMMs to record values.

In conclusion, the deliberate structural distortion of a Mn$_6$ compound via the use of a bulky salicylaldoxime derivative switches the intra-triangular magnetic exchange from antiferromagnetic to ferromagnetic resulting in an S = 12 ground state and an anisotropy barrier ($U_{eff}$) approaching that of the Mn$_{12}$ family. The combined results thus suggest that the intelligent use of ligands that can cause targeted distortions to the core structures of Mn$_6$ (and other) clusters may prove to be a viable means to raise the blocking temperatures of SMMs to record values.

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Supporting Information Available: Crystallographic details in CIF format; synthetic procedures; and magnetism data. This material is available free of charge via the Internet at http://pubs.acs.org.

References


(4) Anal. Calcd (found) for dried 2: C 50.62 (50.78), H 5.14 (5.11), N 4.66 (4.51). Crystal data for 1: 2CH$_2$CH$_2$OH: CaH$_2$OMn$_6$N$_2$O$_8$. FW = 1895.30 g mol$^{-1}$, T = 150 K. Triclinic P, a = 12.4947(9) Å, b = 13.2846(9) Å, c = 14.5047(11) Å, α = 71.488(4)°, β = 82.305(4)°, γ = 68.687(4)°, V = 2126.4(3) Å$^3$, d$_{calc}$ = 1.480 g cm$^{-3}$, independent reflections 11741 [R(int) = 0.034], data 8011, parameters 547, final R1 = 0.0339 for 8011 reflections with $F > 4σ(F)$. Conventional R [R = $4σ(F)]$, R1 = 0.0339 [8011 data].


Figure 2. Plot of reduced magnetization (M/M$_0$) versus H/T for 2 in the field and temperature ranges 0.5–7 T and 1.8–7 K. The solid lines correspond to the fit of the data.

Figure 3. Out-of-phase ($\chi''$) ac susceptibility measurements in the 1.8–8 K and 50–1000 Hz ranges (insert). Arrhenius plot using ac (green) and dc (red) data. The dashed line is the fit of the thermally activated region to eq 2.

$$\hat{H} = D \hat{S}_z^2 + g \mu_B \hat{S} \cdot \hat{H}$$

where $D$ is the axial anisotropy, $\mu_B$ is the Bohr magneton, $\mu_0$ is the vacuum permeability, $\hat{S}_z$ is the easy-axis spin operator, and $\hat{H}$ is the applied field. The best fit gave $S = 12$, $g = 1.99$ and $D = -0.43$ cm$^{-1}$.

Ac susceptibility measurements were performed in the 1.8–16 K range under a 3.5 G ac field oscillating at 50–1000 Hz. The value of the in-phase ($\chi_M$) signal (Figure S3) increases with decreasing temperature to $\sim$6 K, where it then plateaus at $\sim$4 K before displaying a frequency-dependent decrease below this temperature. This is indicative of the presence of excited states of smaller $S$ values relatively close to the ground state. Extrapolation of the in-phase ($\chi_M$) signal to 0 K from the plateau region gives a value of $\sim$74 cm$^{-1}$ indicative of an $S = 12$ ground state, in agreement with the dc data (Figure S3). Fully visible, frequency-dependent out-of-phase ($\chi''$) ac susceptibility signals are seen below $\sim$6 K with the peak at 1000 Hz occurring at $\sim$4.5 K (Figure 3).

Single-crystal hysteresis loop and relaxation measurements were performed on 2 using a micro-SQUID setup. Hysteresis loops were observed whose coercivity was strongly temperature (Figure 4) and sweep-rate (Figure S4) dependent, with a blocking temperature of $\sim$3.5 K. Relaxation data determined from a combination of single-crystal dc and powder ac measurements were fitted to the Arrhenius relationship (eq 2, Figure 3),

$$\tau = \tau_0 \exp(U_{eff}/kT)$$

where $U_{eff}$ is the effective relaxation barrier, $\tau$ is the relaxation time, and $k$ is the Boltzmann constant, giving $U_{eff} = 53.1$ K and $\tau_0 = 8 \times 10^{-10}$ s. The theoretical upper limit of $U = 5|D| = 88.5$ K is strongly reduced by the presence of low-lying excited states as evidenced by the fine structure in the hysteresis loops which are indicative of tunneling between excited-state multiplets. Detailed analyses of these will appear in a full paper.