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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 oximate ligands is fascinating since the exchange in all other complexes containing the $[\text{Mn}^{\text{III}}_3\text{O}]^{7+}$ core, including the well-known “basic carboxylates” of general formula $[\text{Mn}^{\text{III}}_3\text{O}(\text{O}_2\text{-CR})_6\text{L}_3]^+$ ($\text{R} = \text{Me, Et; L} = \text{py, MeCN, etc.}$), is antiferromagnetic.¹ We speculate that a structural distortion in the core of the molecule caused primarily by the “twisting” of the oximate ligands (with regard to the Mn^{III}_3 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 $[\text{Mn}^{\text{III}}_6\text{O}_2(\text{sao})_6(\text{O}_2\text{CPh})_2(\text{EtOH})_4]$ (**1**).² Complex **1**, obtained upon the reaction of $\text{Mn}(\text{O}_2\text{CPh})_2 \cdot 2\text{H}_2\text{O}$ with saoH₂ in EtOH (Figure S1) contains a nonplanar $[\text{Mn}^{\text{III}}_6(\mu_3\text{-O})_2(\mu\text{-OR})_2]^{12+}$ unit of two off-set, stacked $[\text{Mn}^{\text{III}}_3(\mu_3\text{-O})]^{7+}$ triangular subunits linked by two central oximate oxygens, with the remaining four sao²⁻ ligands bridging in a near-planar $\eta^1:\eta^1:\eta^1:\mu$ -fashion along the edges of the $[\text{Mn}^{\text{III}}_3(\mu_3\text{-O})]^{7+}$ 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 μ -carboxylate groups. **1** displays an $S = 4$ spin ground state as a result of ferromagnetic exchange between the two antiferromagnetically coupled Mn^{III}_3 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 Mn_3 triangle¹ and the recently obtained ferromagnetic $[\text{Mn}^{\text{III}}_4(\text{Me-sao})_4(\text{Me-saoH})_4]$ “cube”,³ and thus switch the magnetic behavior from antiferromagnetic to ferromagnetic. Complex $[\text{Mn}^{\text{III}}_6\text{O}_2(\text{Et-sao})_6(\text{O}_2\text{CPh})_2(\text{EtOH})_4(\text{H}_2\text{O})_2] \cdot 2\text{EtOH}$ (**2**·2EtOH) 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 Mn_3 subunit (Figure 1). This is evidenced by the average Mn–N–O–Mn torsion angle, which in **1** is $\alpha_v = 17.5^\circ$ compared to $\alpha_v = 36.5^\circ$ for **2**. This also results in a change in the

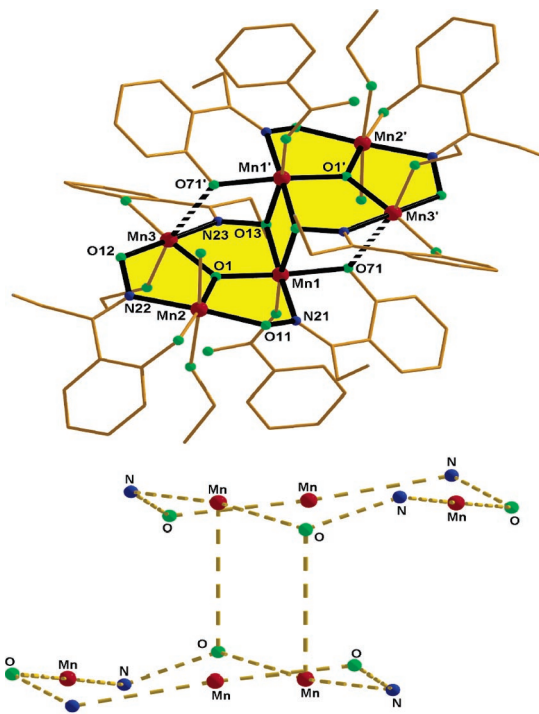


Figure 1. The molecular structure of complex **2**, highlighting its core (top); the “twisted” Mn–N–O–Mn arrangement of the Etsao²⁻ ligands in **2** (bottom).

coordination of the carboxylates: from μ -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 $\chi_{\text{M}}T$ value of $19.24 \text{ cm}^3 \text{ K mol}^{-1}$ is slightly above that expected for six noninteracting Mn^{III} ions ($18 \text{ cm}^3 \text{ K mol}^{-1}$). Upon cooling the value of $\chi_{\text{M}}T$ increases gradually to $23.72 \text{ cm}^3 \text{ K mol}^{-1}$ at ~ 70 K, below which it increases rapidly to a maximum value of $69.57 \text{ cm}^3 \text{ K mol}^{-1}$ at 6.5 K, before decreasing slightly to $69.36 \text{ cm}^3 \text{ K mol}^{-1}$ 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 ($M/N\mu_{\text{B}}$) versus H/T in Figure 2. The data were fit by a matrix diagonalization method to a model that assumes only the ground state is populated, includes axial zero-field splitting ($D\hat{S}_z^2$) and the Zeeman interaction, and carries out a full powder average. The corresponding Hamiltonian is given by eq 1,

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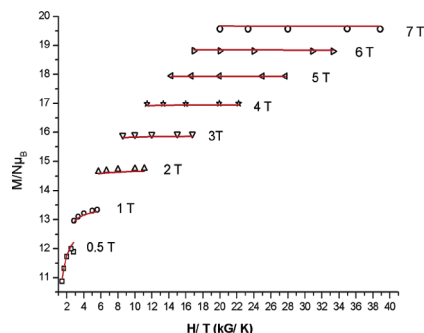


Figure 2. Plot of reduced magnetization ($M/N\mu_B$) versus H/T for **2** in the field and temperature ranges 0.5–7 T and 1.8–7 K. The solid lines correspond to the fit of the data.

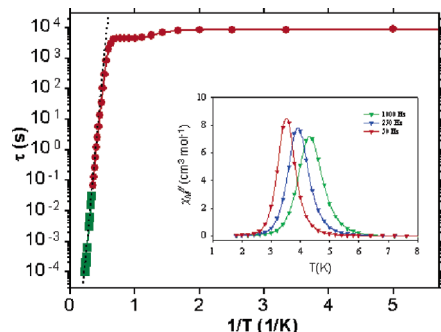


Figure 3. Out-of-phase (χ_M'') ac susceptibility measurements in the 1.8–8 K and 50–1000 Hz ranges (insert); Arrhenius plot using ac (green) and dc (red) data. The dashed line is the fit of the thermally activated region to eq 2.

$$\hat{H} = D\hat{S}_z^2 + g\mu_B\mu_0\hat{S}\cdot H \quad (1)$$

where D is the axial anisotropy, μ_B is the Bohr magneton, μ_0 is the vacuum permeability, \hat{S}_z is the easy-axis spin operator, and H is the applied field. The best fit gave $S = 12$, $g = 1.99$ and $D = -0.43 \text{ cm}^{-1}$.

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 (χ_M') signal (Figure S3) increases with decreasing temperature to ~ 6 K where it then plateaus at ~ 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 (χ_M') signal to 0 K from the plateau region gives a value of $\sim 74 \text{ cm}^3 \text{ K mol}^{-1}$ indicative of an $S = 12$ ground state, in agreement with the dc data (Figure S3). Fully visible, frequency-dependent out-of-phase (χ_M'') ac susceptibility signals are seen below ~ 6 K with the peak at 1000 Hz occurring at ~ 4.5 K (Figure 3).

Single-crystal hysteresis loop and relaxation measurements were performed on **2** using a micro-SQUID setup.⁵ Hysteresis loops were observed whose coercivity was strongly temperature (Figure 4) and sweep-rate (Figure S4) dependent, with a blocking temperature of ~ 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),

$$\tau = \tau_0 \exp(U_{\text{eff}}/kT) \quad (2)$$

where U_{eff} is the effective relaxation barrier, τ is the relaxation time, and k is the Boltzmann constant, giving $U_{\text{eff}} = 53.1 \text{ K}$ and $\tau_0 = 8 \times 10^{-10} \text{ s}$. The theoretical upper limit of $U = S^2|D| = 88.5 \text{ K}$ is strongly reduced by the presence of low-lying excited states as

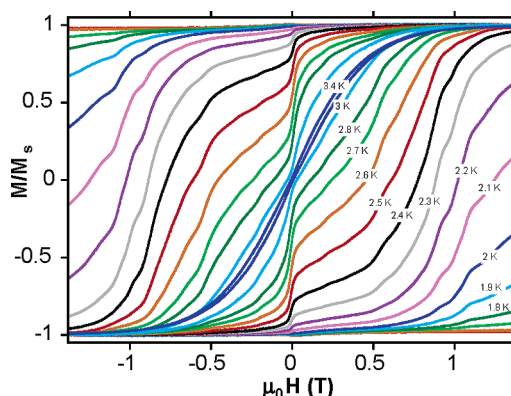


Figure 4. Magnetization versus field hysteresis loops for a single crystal of **2** at the indicated temperatures in a field sweep rate of 0.14 T s^{-1} . M is normalized to its saturation value.

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.

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.^{7,8} 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>.

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