Initial Example of a Triangular Single-Molecule Magnet from Ligand-Induced Structural Distortion of a [Mn$^{III}_3$O]$^{7+}$ Complex

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Single-molecule magnets (SMMs) are individual molecules that function as nanoscale magnetic particles.[1,2] They derive their properties from the combination of a large ground-state spin (S) and a magnetoanisotropy of the Ising-type (negative zero-field splitting parameter, D).[1] They also display quantum tunneling of magnetization (QTM)[3] and quantum phase interference,[4] properties of the microscale. SMMs of various types and metal topologies are now known, with most being Mn species. There are, however, no triangular SMMs; numerous oxide-centered triangular [M$_3$O(O$_2$-CR)$_6$L$_3$]$^{n+}$ ($n = 0$, 1) complexes are known for many transition metals,[5a] but antiferromagnetic exchange interactions within the [M$_3$O] core lead to small S values, and they are therefore not SMMs.[5] It is thus tempting to conclude that this common triangular [M$_3$O] structural topology can never lead to SMMs, but we show in the present work that relatively small, ligand-imposed structural distortions can alter the sign of the exchange interactions and "switch on" the SMM property.

We have been exploring the use of 2-pyridyl oximes[6] in the synthesis of 3d metal clusters, and we can now report that methyl 2-pyridyl ketone oxime (mpkoH) has yielded a new triangular [Mn$^{III}_3$O] product. This is very unusual in being ferromagnetically coupled with a resultant $S = 6$ ground-state spin and is indeed the first triangular SMM.

The reaction of [Mn$_3$O(O$_2$CMe)$_6$(py)$_3$](ClO$_4$) (**1**) with mpkoH (3 equiv) in MeOH/MeCN (1:2 v/v) gave a dark-brown solution. This was evaporated to dryness under reduced pressure, and the residue was dissolved in CH$_2$Cl$_2$ and layered with *n*-hexane. After 2 days, dark-brown crystals of [Mn$_3$O(O$_2$CMe)$_3$(mpko)$_3$](ClO$_4$)· ·3CH$_2$Cl$_2$ (**2**·3CH$_2$Cl$_2$) were isolated in 80–90% yield. The structure[7] of **2**·3CH$_2$Cl$_2$ (Figure 1) consists of a near-equilateral Mn$^{III}_3$ triangle capped by μ_3-O^{2-} ion O61. Each edge is bridged by an η^1:η^1:μ-MeCO$_2^-$ group and an η^1:η^1:η^1:μ-mpko$^-$ group, whose pyridyl ring is bound terminally to a Mn. O61 is 0.295 Å above the Mn$_3$ plane. The Mn^{III} oxidation states and O^{2-} protonation level were established by bond valence sum (BVS) calculations,[8,9] charge considerations, and the presence of Mn^{III} Jahn–Teller elongation axes (O1–Mn1–O31, O11–Mn2–O51, O21–Mn3–O42). The isostructural propionate analogue was prepared in an identical manner.

Variable-temperature DC magnetic susceptibility data were collected on dried **2** in the temperature range of 5.0–300 K in an applied field of 1 kG (0.1 T). $\chi_M T$ is 13.01 cm^3 mol^{-1} K at 300 K, increasing on cooling to a maximum of 19.39 cm^3 mol^{-1} K at 30.0 K, and then decreasing to 17.41 cm^3 mol^{-1} K at 5.00 K.[9] This indicates ferromagnetic exchange interactions within **2** to give an $S = 6$ ground state, which is consistent with the 30.0 K value (spin-
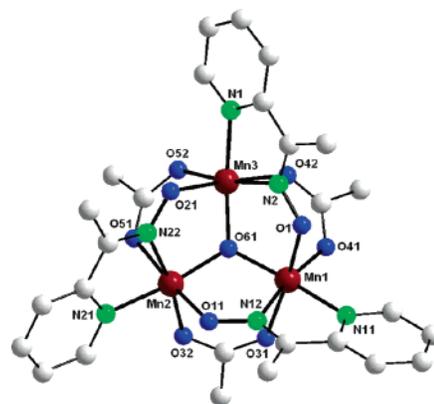
Figure 1. Molecular structure of **2**. Color code: brown, manganese; blue, oxygen; green, nitrogen; gray, carbon.
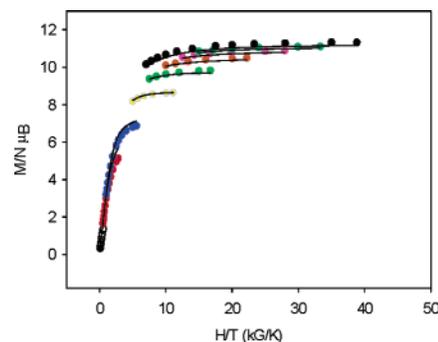
Figure 2. Plot of $M/N\mu_B$ versus H/T for complex **2** at 7 (black dot), 6 (dark green dot), 5 (magenta dot), 4 (orange dot), 3 (light green dot), 2 (yellow dot), 1 (blue dot), 0.5 (red dot), and 0.1 (open dot) tesla. The solid lines are the fit of the data.

only ($g = 2$) value for $S = 6$ is 21 cm^3 mol^{-1} K). The low temperature decrease is assigned to Zeeman effects, zero-field splitting, and/or weak intermolecular interactions. The data were fit to the theoretical expression for a 3Mn^{III} isosceles triangle.[9,10]

To confirm the ground state of **2**, magnetization (M) data were collected in the 0.1–7 T and 1.8–10.0 K ranges, and these are plotted as $M/N\mu_B$ versus H/T in Figure 2. The data were fit by matrix-diagonalization 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 spin Hamiltonian is given by eq 1, where μ_B is the Bohr magneton and μ_0 is the vacuum permeability, $\hat{S}_z$

$$H = D\hat{S}_z^2 + g\mu_B\mu_0\hat{S}_z H_z \qquad (1)$$
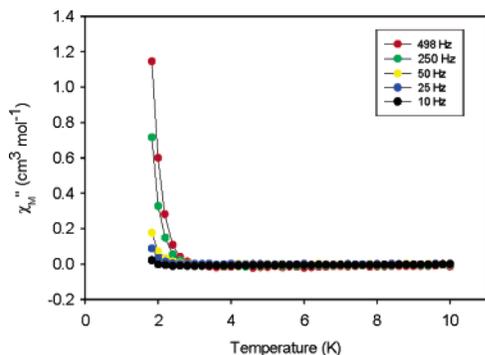
is the easy-axis spin operator, and H_z is the applied field. The fit (solid lines in Figure 2) gave $S = 6$, $g = 1.92$, and $D = -0.34$ cm^{-1}.[11]
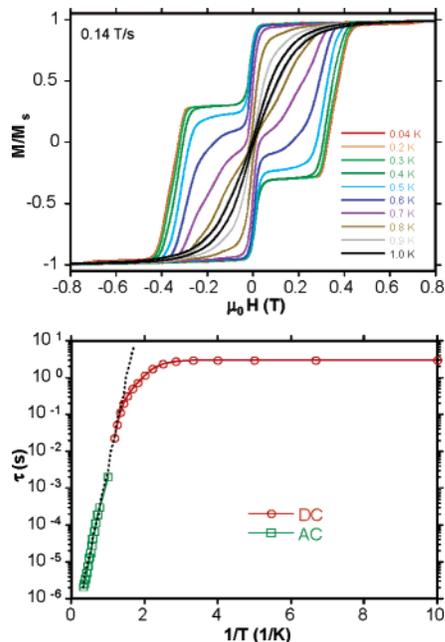
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Figure 3. Plot of the out-of-phase (χ_M'') AC susceptibility signal versus temperature for a microcrystalline sample of complex **2**.

Figure 4. (Top) Magnetization versus field hysteresis loops for a single crystal of **2·3CH₂Cl₂** at the indicated temperatures; M is normalized to its saturation value, M_S. (Bottom) Arrhenius plot constructed from AC χ_M'' versus T and DC magnetization decay versus time data. The dashed line is the fit of the thermally activated region to the Arrhenius equation.

Since **2** has significant S and D values, we investigated whether it is a SMM by AC susceptibility measurements in a 3.5 G AC field (Figure 3). Indeed, a frequency-dependent decrease in the in-phase ($\chi_M'T$) signal[9] and a concomitant out-of-phase (χ_M'') signal were seen at <3 K (Figure 3), indicative of the slow magnetization relaxation of SMMs. Since intermolecular interactions and phonon bottlenecks can also give such signals,[12] confirmation that **2** is a SMM was sought by magnetization versus DC field scans on single crystals of **2·3CH₂Cl₂** using a micro-SQUID.[13] Hysteresis, the diagnostic property of a magnet, was observed below ~1.0 K (Figure 4, top). The loops exhibit increasing coercivity with decreasing temperature and increasing field sweep rate,[9] as expected for a SMM. The loops also display the steps indicative of QTM between M_S levels of the $S = 6$ ground state, with the temperature independent coercivity at ≤0.3 K, indicating ground state QTM, that is, only between the lowest energy $M_S = \pm 6$ levels.

AC data to lower T and magnetization decay versus time data were collected and used to construct Figure 4 (bottom), based on the Arrhenius relationship $\tau = \tau_0\exp(U_{eff}/kT)$, where U_{eff} is the effective relaxation barrier, τ is the relaxation time, and k is the Boltzmann constant. The slope in the thermally activated region gave $U_{eff} = 10.9$ K and $\tau_0 = 5.7 \times 10^{-8}$ s. Below 0.3 K, the

relaxation was temperature-independent, consistent with relaxation by ground-state QTM.

Complex **2** is thus confirmed to be a SMM, the first with a triangular topology. What now demands explanation is why **2** is ferromagnetically coupled and a SMM whereas the many previous triangular [Mn₃O(O₂CR)₆L₃]⁺ complexes (such as **1**) are antiferromagnetically coupled and are not? We believe the answer is that **2** has its central O^{2-} ion 0.295 Å above the Mn₃ plane due to the tridentate binding of the mpko⁻ ligand, whereas the O^{2-} ion in **1** and related species is in the Mn₃ plane, or essentially so (<0.03 Å). The central O^{2-} strongly mediates antiferromagnetic exchange via $M_{d\pi}-O_{p\pi}-M_{d\pi}$ orbital overlap, and any distortion away from planarity will thus weaken antiferromagnetic contributions to the observed exchange, J_{obs}, between two Mn atoms. Since J_{obs} is the sum of ferro- and antiferromagnetic contributions, and J_{obs} is in any case only weakly antiferromagnetic in [Mn₃O(O₂CR)₆L₃]⁺ complexes,[5] it is reasonable that structural distortion to a nonplanar [Mn₃O]⁷⁺ core would lead to ferromagnetic J_{obs} and a resultant $S = 6$ ground state.[14]

In conclusion, the distortion imposed on a [Mn₃O]⁷⁺ member of the venerable class of triangular, oxide-centered [M₃O]⁶⁺,⁷⁺ complexes by a tridentate oximate ligand switches the exchange coupling to ferromagnetic and makes **2** the initial example of a triangular SMM. This suggests that it may also be possible to modify other triangular (or other) structures with chelating and/or bridging ligands to switch on the properties of a SMM.

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

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(7) Anal. Calcd (found) for dried **2** (solvent-free): C 37.59 (37.32), H 3.50 (3.49), N 9.74 (9.54). Crystal data for **2·3CH₂Cl₂**: C₃₃H₃₆N₆O₁₄Cl₇Mn₃, 1117.54 g mol⁻¹, monoclinic $P2_1/c$, $a = 12.986(5)$ Å, $b = 14.978(6)$ Å, $c = 23.150(10)$ Å, $\beta = 93.82(2)°$, $Z = 4$, $V = 4493(3)$ Å³, $d_{calcd} = 1.492$ g cm⁻³, $T = 293(2)$ K. Final $R1 = 6.96$ and $wR2 = 19.36\%$.
(8) (a) Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993**, *32*, 4102−4105. (b) BVS for the Mn³⁺ and O²⁻ ions were 3.03−3.12 and 2.08, respectively.
(9) See Supporting Information.
(10) The fit gave $J = +14.1$ cm⁻¹, $J' = +3.8$ cm⁻¹, $g = 1.91$, and 0.9% paramagnetic impurity term; the TIP was held constant at 600×10^{-6} cm³ mol⁻¹. Equilateral [M₃O] triangles undergo the magnetic Jahn−Teller distortion, resulting in an isosceles (2J) situation. See: Cannon, R. D.; Jayasooriya, U. A.; Wu, R.; arapKoske, S. K.; Stride, J. A.; Nielsen, O. F.; White, R. P.; Kearley, G. J.; Summerfields, D. *J. Am. Chem. Soc.* **1994**, *116*, 11869−11874 and references therein.
(11) The fit for the propionate analogue of **2** gave $S = 6$, $g = 1.93$, and $D = -0.34$ cm⁻¹; this complex gives the same ac susceptibility data as **2**.
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(14) The D value will also be affected by this distortion, as the single-ion anisotropy axes are tilted. Details will be provided in the full paper.

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