

Template Synthesis and Single-Molecule Magnetism Properties of a Complex with Spin $S = 16$ and a $[\text{Mn}_8\text{O}_8]^{8+}$ Saddle-Like Core

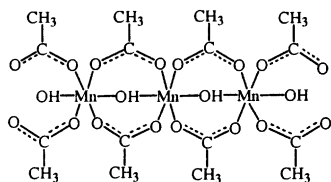
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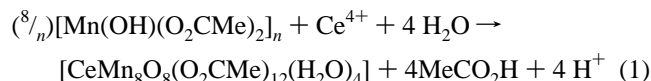
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Single-molecule magnets (SMMs) represent a molecular approach to nanoscale magnetic materials.^{1–3} A SMM derives its properties from a combination of a large ground-state spin (S) value and an Ising (easy-axis) type of magnetoanisotropy (negative zero-field splitting parameter, D). Several types of SMMs are now known, most of them containing Mn^{III} , but there is continuing need for novel structural types to enlarge the available database and thus improve our understanding of this interesting phenomenon.^{1–5} In the present work, we report two discoveries: (i) a template-based procedure that cleanly converts a Mn^{III} chain polymer to a molecular loop complex, a prototype of a valuable new potential methodology for accessing loop species with Mn and other metals and (ii) the establishment that this complex is a SMM with an $S = 16$ ground state, the highest yet for a Mn species.

$[\text{Ce}^{\text{IV}}\text{Mn}^{\text{III}}_8\text{O}_8(\text{O}_2\text{CMe})_{12}(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ (**1**· $4\text{H}_2\text{O}$) was originally obtained by accident in low yield from a solution of $[\text{Ce}^{\text{IV}}\text{Mn}^{\text{IV}}_6\text{O}_9(\text{O}_2\text{CMe})_9(\text{NO}_3)(\text{H}_2\text{O})_2]$ (**2**)⁶ in MeCN/Et₂O that had stood for a long time. With the identity of **1** established, a rational synthesis was considered crucial. Truly targeted syntheses of large metal loops are a great challenge, such species typically being obtained serendipitously,⁷ but we successfully developed a targeted route to **1** using a template approach. The strategy was to use the oxophilic Ce^{4+} ion as the template around which might wrap the linear Mn^{III} polymer $\{[\text{Mn}^{\text{III}}(\text{OH})(\text{O}_2\text{CMe})_2] \cdot (\text{MeCO}_2\text{H}) \cdot (\text{H}_2\text{O})\}_n$ (**3**)⁸ as $\text{Ce}^{4+}-\text{OH}^-$ contacts developed. With a Ce:Mn ratio of 1:8 and OH^- deprotonation, this encirclement could in principle give **1**, since **3** provides all the required components; the chain structure of **3** is shown below.



Indeed, treatment of an MeCN slurry of insoluble **3** with 0.125 equiv of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and stirring for 8 h led to slow dissolution of **3** and the formation of a brown solution. Filtration, addition of Et₂O, and slow concentration by evaporation led to crystallization of **1**· $4\text{H}_2\text{O}$ in 55% isolated yield (eq 1).⁹



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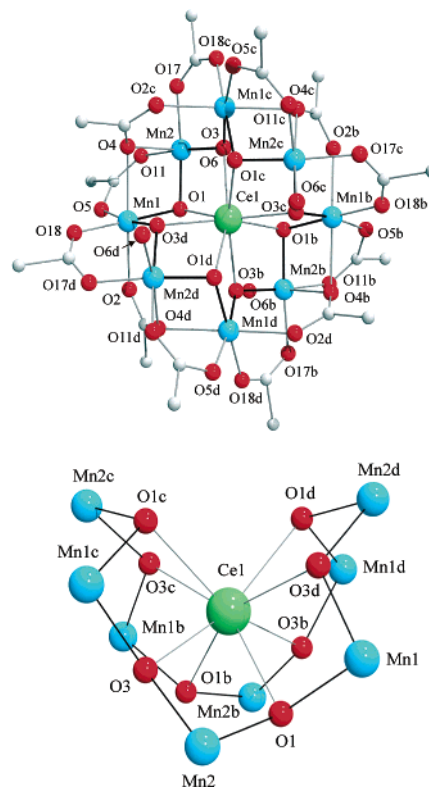


Figure 1. Labeled PovRay plot of **1** (top), and its $[\text{CeMn}_8\text{O}_8]^{12+}$ core emphasizing the saddle-like folding of the $[\text{Mn}_8\text{O}_8]$ ring (bottom).

The structure of **1** (Figure 1)⁹ consists of a nonplanar, saddle-like $[\text{Mn}_8\text{O}_8]^{8+}$ loop attached to the central Ce^{4+} via the O^{2-} ions. Charge considerations, metric parameters, bond valence sums, and Mn^{III} Jahn–Teller (JT) elongation axes establish a $\text{Ce}^{\text{IV}}\text{Mn}^{\text{III}}_8$ situation.¹⁰ Eight *syn, syn*, doubly- and four triply-bridging acetate groups and four terminal water molecules provide the peripheral ligation. The molecule has crystallographic S_4 symmetry. Interestingly, the $[\text{Mn}_8\text{O}_8]$ loop is very similar to that in $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$ (**4**), which has a central $[\text{Mn}_4\text{O}_4]$ cubane instead of the smaller Ce atom.² The eight $\text{Ce}^{4+}-\text{O}^{2-}$ bonds are undoubtedly crucial to the formation of **1** and cause a greater folding of the $[\text{Mn}_8\text{O}_8]$ ring than in **4**. The Ce–O bond lengths (2.29–2.37 Å) are typical for eight-coordinate Ce^{IV} .^{10c} The Mn^{III} JT elongation axes are $\text{O}(2)-\text{Mn}(1)-\text{O}(4)$ and $\text{O}(4)-\text{Mn}(2)-\text{O}(6)$, meeting at $\text{O}(4)$ almost at right angles ($\text{Mn}(1)-\text{O}(4)-\text{Mn}(2) = 83.9(8)^\circ$). The four $\text{Mn}(2)$ atoms occupy the corners of an almost perfect tetrahedron ($\text{Mn}(2)-\text{Ce}(1)-\text{Mn}(2c) = 109.43(4)^\circ$), whereas the four $\text{Mn}(1)$ atoms form a severely distorted (flattened) tetrahedron ($\text{Mn}(1)-\text{Ce}(1)-\text{Mn}(1c) = 92.02(4)^\circ$). The Ce^{IV} ion is at the center

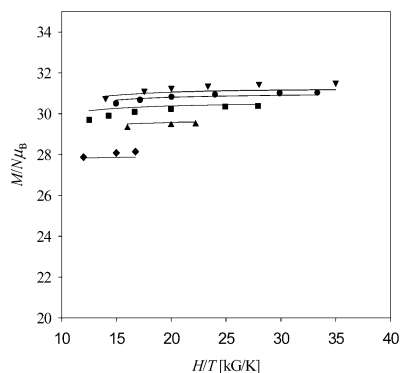


Figure 2. Plot of reduced magnetization, $(M/N\mu_B)$ vs H/T for **1** at 70 (▼), 60 (●), 50 (■), 40 (▲), and 30 (◆) K. The solid lines are the fit; see the text for the fitting parameters.

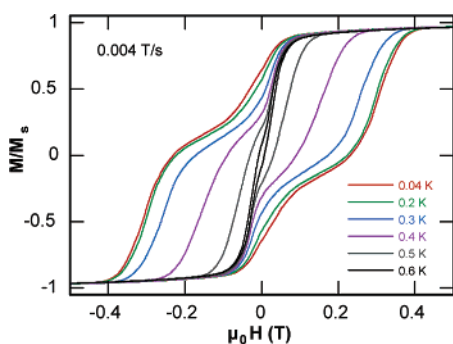


Figure 3. Magnetization (M) vs magnetic field hysteresis loops for **1** at the indicated temperatures. M is normalized to its saturation value, M_s .

of both tetrahedra. There are strong inter- and intramolecular hydrogen-bonding interactions involving the lattice and bound water molecules, as well as O atoms from oxide and carboxylate ligands.

Solid-state DC magnetic susceptibility (χ_M) data were collected in the 5.0–300 K range in a 5.0 kG field. The $\chi_M T$ value of 32.3 $\text{cm}^3 \text{K mol}^{-1}$ at 300 K is higher than the 24 $\text{cm}^3 \text{K mol}^{-1}$ for eight noninteracting Mn^{III} centers (Ce^{IV} is diamagnetic, f^0), and increases steadily to 61.3 $\text{cm}^3 \text{K mol}^{-1}$ at 6.5 K before decreasing slightly to 59.5 $\text{cm}^3 \text{K mol}^{-1}$ at 5.0 K. This suggests ferromagnetic interactions within the molecule and a large ground-state spin value. The latter was determined from magnetization (M) data collected in the 1.8–5.0 K and 30–70 kG ranges. The data were fit assuming only the ground state is populated and including axial zero-field splitting ($D\hat{S}_z^2$) and Zeeman interactions. The fit (solid lines in Figure 2) gave $S = 16$, $D = -0.10(1) \text{ cm}^{-1}$, and $g = 1.98(1)$. Ferromagnetic coupling thus aligns the eight Mn^{III} spins parallel, as in **4**, and **1** consequently has the largest S value yet seen for a Mn_x cluster, almost equal to the $S = 33/2$ of an Fe_{19} cluster.⁵

An $S = 16$ ground state and a negative D suggested that **1** might have a sufficient barrier to magnetization relaxation to be an SMM. This was explored on single crystals of $\mathbf{1}\cdot\mathbf{4H}_2\mathbf{O}$ using a micro-SQUID,¹¹ and M vs DC field sweeps are shown in Figure 3. Hysteresis loops are evident below ~ 0.6 K, their coercivities increasing with decreasing temperature, as expected for an SMM. The two-step profile and its variation with T are characteristic of a weak intermolecular interaction between molecules, undoubtedly mediated by the hydrogen bonds and dipolar interactions; similar behavior is seen in the Fe_{19} SMMs.⁵ This interaction only perturbs

the SMM; it is too weak to give a classical, antiferromagnetically ordered network. An intermolecular exchange parameter (J) of only 0.0025 K and an interaction energy of 0.65 K can be calculated from the loops. The low temperature at which **1** is a SMM is clearly due to the small D value, which is consistent with some of the Mn^{III} JT axes, the primary source of the molecular anisotropy, being nearly perpendicular. The upper limit to the relaxation barrier is $S^2|D| = 25.6 \text{ cm}^{-1}$ for **1**, but the effective barrier will be significantly less due to quantum tunneling through the barrier.

In summary, a template procedure has allowed a good yield of a new molecular CeMn_8 cluster to be obtained from a linear Mn^{III} polymer. This new procedure has great potential as a route to related species by replacing the Mn for other metal ions or the Ce for other templating metal ions or groups. Complex **1** has the largest spin yet discovered for a Mn cluster and represents the first loop-based Mn SMM. The largest S value for any molecular metal cluster is currently $S = 51/2$ in a heterometallic $\text{Mn}^{\text{II}}/\text{Mo}^{\text{V}}$ system, which is not a SMM, however.¹² Derivatives of **1** are being sought with more bulky carboxylates to block the intermolecular interactions and allow better study of the quantum tunneling in this distinctly new type of Mn SMM. Various methods are also under investigation to flatten the $[\text{Mn}_8\text{O}_8]$ loop into a more planar conformation; with the JT axes more parallel, the D value will approach that in **4**, and the barrier to relaxation should be dramatically increased.

Acknowledgment. This work was supported by the National Science Foundation.

Supporting Information Available: Crystallographic details (CIF) for $\mathbf{1}\cdot\mathbf{4H}_2\mathbf{O}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (a) Anal. Calcd (Found) for $\mathbf{1}\cdot\mathbf{4H}_2\mathbf{O}$: C 18.47 (18.49), H 3.36 (3.32). (b) Crystal data for $\mathbf{1}\cdot\mathbf{4H}_2\mathbf{O}$: $\text{C}_{24}\text{H}_{52}\text{O}_{40}\text{Mn}_8\text{Ce}$, 1560.30 g mol^{-1} , tetragonal $I4$, $a = 23.947(6) \text{ \AA}$, $c = 9.953(5) \text{ \AA}$, $Z = 4$, $V = 5708(4) \text{ \AA}^3$, $d_{\text{calc}} = 1.816 \text{ g cm}^{-3}$, $T = 100 \text{ K}$. Final $R1 = 8.99$ and $wR2 = 21.63\%$. The crystal was a small, thin plate; an absorption correction was applied.
- (a) Bond valence sum calculations for the Mn^{10b} and Ce^{10c} ions of **1** gave oxidation state values of 2.84–3.03 and 3.73–3.96, respectively. (b) Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993**, 32, 4102. (c) Roulhac, P. L.; Palenik, G. J. *Inorg. Chem.* **2003**, 42, 118.
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JA0385134