

Isomeric Forms of $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$ Single-Molecule MagnetsZiming Sun,^{1a} Daniel Ruiz,^{1a} Evan Rumberger,^{1a} Christopher D. Incarvito,^{1b} Kirsten Foltling,^{1c} Arnold L. Rheingold,^{1b} George Christou,^{*,1c} and David N. Hendrickson^{*,1a}

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The interest in single-molecule magnets (SMMs) is increasing dramatically.^{2–7} As a result of a large-spin ground state and significant magnetoanisotropy, a SMM exhibits magnetization relaxation phenomena such as a magnetization hysteresis loop. The first complex discovered to be a SMM is $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]\cdot\text{S}$ (**1**), where R is CH₃ and S is 2(CH₃CO₂H)·4(H₂O).³ Each Mn₁₂ molecule has an appreciable potential-energy barrier for reversal of the direction of its magnetization vector. The increasingly active study of SMMs is driven by two goals.⁴ First, an array of SMMs could serve as the ultimate high-density memory device. Second, for several decades scientists have tried to characterize quantum magnetization tunneling (QMT) for nanomagnets. In fact, Friedman et al.⁵ first reported in 1996 that Mn₁₂ complex **1** exhibits steps on its hysteresis loop that are due to QMT. Since then, complex **1** has attracted the attention of many physicists.^{5,6} In this communication we report the characterization of new Mn₁₂ SMMs that give insight into the mechanism of magnetization relaxation in these fascinating molecules.

When the temperature of a sample of a Mn₁₂ SMM is low relative to the kinetic barrier for reversal of magnetization direction, the frequency of an ac SQUID susceptometer can be varied and a maximum in the out-of-phase ac susceptibility (χ''_M) is seen when the frequency equals the rate of magnetization reversal. Complex **1** shows essentially one χ''_M peak, whereas we have found^{2c} that other Mn₁₂ complexes generally show two χ''_M peaks in the 2–4 and 4–7 K regions. The observation of two χ''_M peaks is interesting and it is important to understand the factors that control this phenomenon because the χ''_M peak positions reflect the rate of magnetization relaxation.⁷

In our previous paper⁷ we reported two different crystallographic forms of $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_6\text{H}_4\text{-}p\text{-Me})_{16}(\text{H}_2\text{O})_4]\cdot\text{S}$ (**2**) that differ in the solvate molecules S in each crystal, and in the arrangement of the 4 H₂O and 16 *p*-methylbenzoate ligands, raising the possibility that the spin S may be affected by these differences in ligand positions. There are two different sets of four Mn^{III} ions bridged by O²⁻ ions to the central $[\text{Mn}^{\text{IV}}_4\text{O}_4]^{8+}$ cubane unit. The H₂O ligands bind only to one set of four Mn^{III} ions and this leads to 11 possible isomeric forms with regard to the H₂O positions. Complex **2a** with S = 3H₂O shows predominantly a χ''_M peak in the 4–7 K region, whereas complex **2b** with S = HO₂CC₆H₄-*p*-Me has a χ''_M peak in the 2–4 K region. The different isomeric arrangements of ligands in **2a** and **2b** could lead to different ground states, S = 10 for complex **2a** and S = 9 ground state for complex **2b**. However, to better evaluate this possibility for the origin of the two χ''_M peaks it was important to characterize other Mn₁₂ SMMs that have different isomeric arrangements of H₂O and carboxylate ligands. Two new SMMs have been characterized: $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{C}_6\text{H}_5)_{16}(\text{H}_2\text{O})_4]$ (**3**) and $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Bu}^t)_{16}(\text{H}_2\text{O})_4]$ (**4**), and their X-ray structures^{8,9} were determined (Figure 1). The $[\text{Mn}_{12}\text{O}_{12}]^{16+}$ cores of these two complexes are essentially superimposable on the cores of complex **1** and **2**. Each $[\text{Mn}_{12}\text{O}_{12}]^{16+}$ core has a central $[\text{Mn}^{\text{IV}}_4\text{O}_4]^{8+}$ cubane held within a nonplanar ring of eight Mn^{III} ions by eight $\mu_3\text{-O}^{2-}$ ions. Complex **1** has a 1:1:1 arrangement of H₂O ligands, i.e., one H₂O ligand on each Mn^{III} ion in one set of 4 Mn^{III} ions. Complex **2a** has a 1:1:2 arrangement of H₂O ligands (one Mn^{III} ion does not have a H₂O ligand), whereas complex **2b** has 1:2:1 arrangement. It was interesting to find that complexes **3** and **4** also have the 1:2:1 arrangement of the four H₂O ligands. In all four complexes the Mn₁₂ molecules are packed in the crystal in a parallel fashion.

Figure 2 shows the out-of-phase ac susceptibility signals obtained for complexes **3** and **4** at frequencies of 1000, 250, and 50 Hz. Complex **3** shows a χ''_M peak in the 4–7 K region. On the other hand, complex **4** shows predominantly a 2–4 K peak with a smaller peak in the 4–7 K range. Thus, it is not simply the isomeric arrangement of four H₂O and 16 carboxylate ligands that determines the magnetization relaxation processes in these

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- (8) Crystal data for **3**: C₁₂₈H₁₂₀Cl₂Mn₁₂O₄₈, 3085.64 g mol⁻¹, triclinic, $P\bar{1}$, $a = 18.1342(4)$ Å, $b = 20.6379(4)$ Å, $c = 20.9134(4)$ Å, $\alpha = 65.545(2)^\circ$, $\beta = 69.088(2)^\circ$, $\gamma = 80.623(2)^\circ$, $Z = 2$, $V = 6654.3(2)$ Å³, $d_{\text{calc}} = 1.415$ mg/m³, and $T = 223(2)$ K. The structure was solved (SHELXTL), $R(F) = 10.38\%$ for 27 877 observed independent reflections ($4 \leq 2\theta \leq 56^\circ$). Two benzyl groups and a third phenyl ring were not located due to the limited resolution of the data and apparent positional disorder. All other phenyl rings were refined as rigid planar groups to conserve data.
- (9) Crystal data for **4**: CH₂Cl₂·CH₃NO₂; C₉₈H₁₈₉Cl₂Mn₁₂NO₅₀, 2911.71 g mol⁻¹, triclinic, $P\bar{1}$, $a = 16.422(2)$ Å, $b = 27.434(3)$ Å, $c = 15.814(2)$ Å, $\alpha = 101.78(1)^\circ$, $\beta = 101.79(1)^\circ$, $\gamma = 76.90(1)^\circ$, $Z = 2$, $V = 6699$ Å³, $d_{\text{calc}} = 1.4444$ mg/m³, and $T = 99$ K. The structure was solved (SHELXTL) and refined on F using 10 081 unique reflections with $F > 2.336(F)$ to R and R_w values of 0.0725 and 0.0563, respectively. No disorder problems were encountered in the Mn₁₂ or solvate molecules.

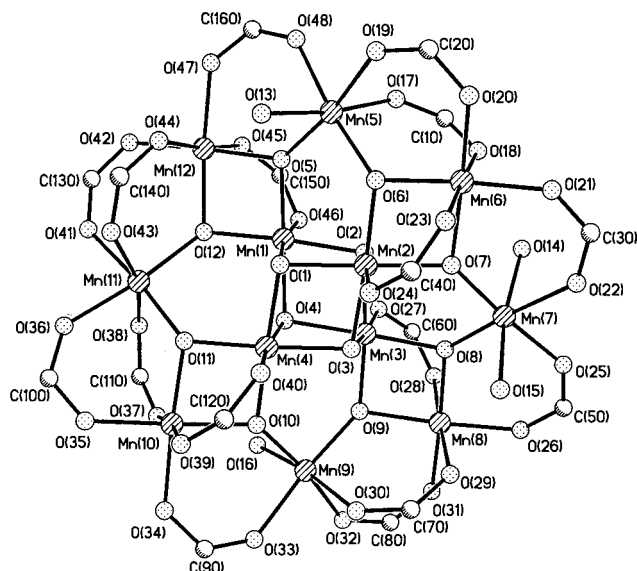


Figure 1. ORTEP representation of the core of the Mn_{12} complex in $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{C}_6\text{H}_5)_{16}(\text{H}_2\text{O})_4]$ (**3**). The O(13), O(14), O(15), and O(16) oxygen atoms correspond to the H_2O ligands.

Mn_{12} complexes. Each SMM has a double potential-energy well, where the lowest energy level on the left corresponds to a Mn_{12} molecule with “spin-up” and the lowest energy level on the right corresponds to the molecule with “spin-down”. Quantized m_s levels result from zero-field splitting (DS_z^2) of the $S = 10$ ground state. For complex **1**, the barrier height is 50 cm^{-1} and it has been shown⁶ that when complex **1** is held at temperatures below 10 K the complex reverses its direction of magnetization vector by quantum mechanical tunneling through the barrier. This occurs via an Orbach phonon process. A Mn_{12} molecule “picks up” phonon energy and is excited to a higher-energy level, say the $m_s = -3$ level. It then tunnels through to the $m_s = +3$ level.

There seems to be three possible origins for the two different kinetic barriers seen in the two different χ''_{M} ac signals for Mn_{12} SMMs. First, the different complexes could have different S and D values for their ground states. There has been some evidence for $S = 10$ and $S = 9$ Mn_{12} complexes from variable-field magnetization studies.^{2c} However, it is difficult to determine the S value to any better than ± 1 using magnetic susceptibility data for these Mn_{12} complexes. The $\chi''_{\text{M}}T$ vs temperature plateau at low temperatures for **4** is somewhat lower in value than that for **3**, in keeping with a lower S value for **4**. High-field EPR data are needed. The second possible origin for different kinetic barriers lies in different tunneling channels. If two different Mn_{12} complexes have the same $S = 10$ ground state (see figure in synopsis), it could be that one has a tunneling channel of $m_s = \pm 3$ whereas the other tunnels on the lower-energy $m_s = \pm 4$ levels. The rate of tunneling is determined by transverse magnetic fields (either external or internally within the molecule, as from nuclear spins) or by transverse higher-order zero-field interaction terms.

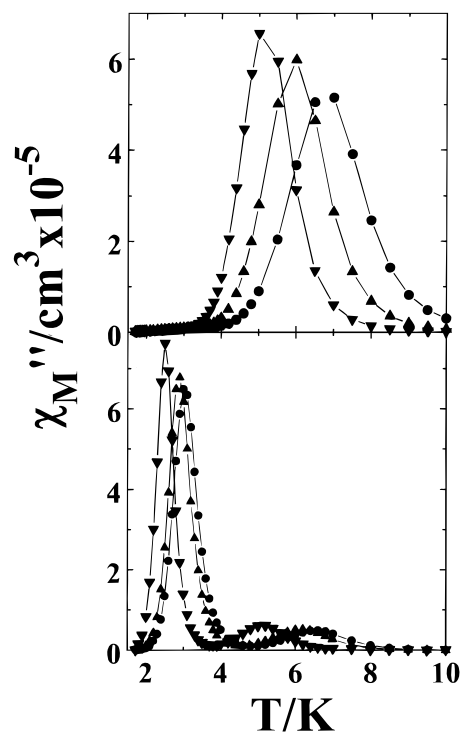


Figure 2. Plot of χ''_{M} vs temperature for $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{C}_6\text{H}_5)_{16}(\text{H}_2\text{O})_4]$ (**3**) (upper) and $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Bu})_{16}(\text{H}_2\text{O})_4]$ (**4**) (lower) in an ac field of 1 G oscillating at 50 Hz (●), 250 Hz (▲), or 1000 Hz (▼).

The third possible origin for different kinetic barriers for tunneling in Mn_{12} SMM lies in the energy ordering of the “spin-ladder” in the different complexes. From one Mn_{12} complex to another, the energy spacing to the first excited spin state may be varying considerable. It is possible that for some Mn_{12} complexes there is a low-energy excited state with a different spin than the ground state. This would introduce a second double well nested on top of the ground-state double well. An Orbach process could excite the Mn_{12} SMM from the $m_s = -10$ level of the ground state to some level in the excited state double well and the complexes would tunnel with a different effective barrier. Inelastic neutron scattering experiments are planned for several Mn_{12} molecules to see if the energy ordering of excited spin states is different from one SMM to another.

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Supporting Information Available: Two X-ray crystallographic files, in CIF format, are available for complexes **3** and **4** on the Internet only. Access information is given on any current masthead page.

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