

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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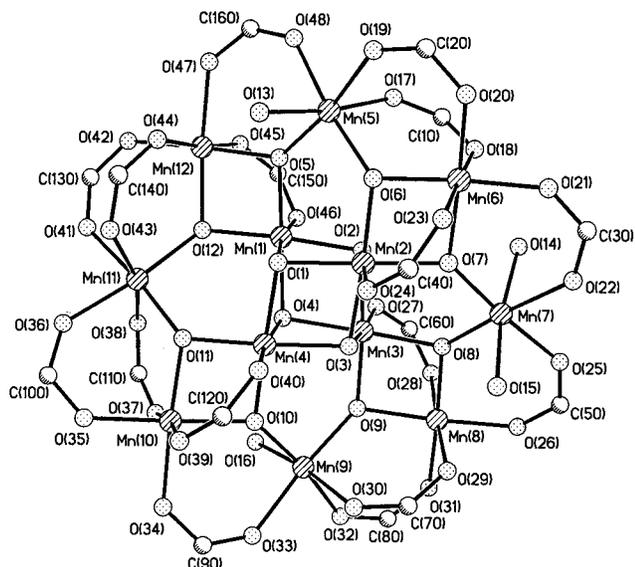


Figure 1. ORTEP representation of the core of the Mn_{12} complex in $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{C}_6\text{H}_5)_{16}(\text{H}_2\text{O})_4]$ (**3**). The O(13), O(14), O(15), and O(16) oxygen atoms correspond to the H_2O ligands.

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.

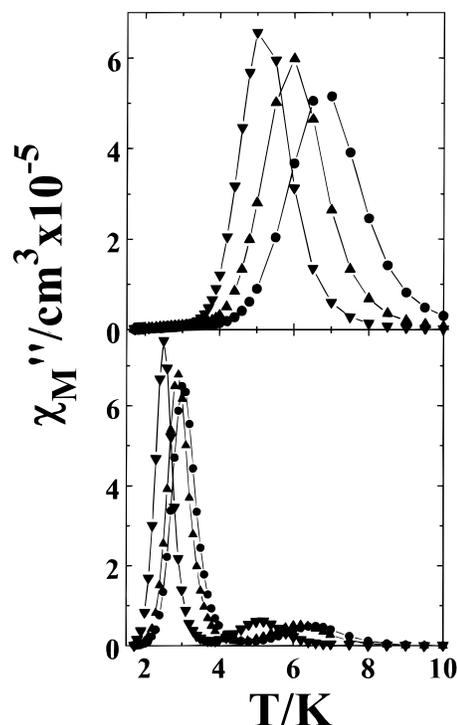


Figure 2. Plot of χ''_{M} vs temperature for $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{C}_6\text{H}_5)_{16}(\text{H}_2\text{O})_4]$ (**3**) (upper) and $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Bu})_{16}(\text{H}_2\text{O})_4]$ (**4**) (lower) in an ac field of 1 G oscillating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

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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