

Isomeric Forms of $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$ Complexes Showing Different Magnetization Relaxation Processes

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The characterization of two new single-molecule magnets, $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{C}_6\text{H}_5)_{16}(\text{H}_2\text{O})_4]$ (**7**) and $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Bu}^t)_{16}(\text{H}_2\text{O})_4]$ (**8**) is reported here. Even though the two complexes have the same isomeric arrangement of H_2O ligands the ac magnetic susceptibility responses are different for the two complexes. Complex **7** shows an out-of-phase (χ_M'') peak in the 4–7 K region, whereas complex **8** shows a χ_M'' peak in the 2–4 K region. The influence of solvate molecules upon the magnetization relaxation rates of these Mn_{12} complexes is studied.

INTRODUCTION

The interest in single-molecule magnets (SMM's) is increasing dramatically.¹⁻¹¹ The discovery of slow magnetization relaxation processes in metal clusters represented an exciting break through for a number of reasons: 1) metal clusters are normally prepared by solution methods and, once purified, are composed of a single, sharply-defined size; 2) they are readily amenable to variations in peripheral carboxylate

ligation (small vs. bulky, hydrophilic vs. hydrophobic, etc.); 3) they are normally soluble in common solvents providing advantages in potential applications; 4) since each molecule has nanoscale dimensions, each molecule could potentially be used in storing a large density of information; and 5) from a theoretical point of view, understanding the magnetic properties of these molecules is important as it will help to bridge the gap between the quantum and classical understanding of magnetism. Three families of complexes that function as SMM's have been obtained: i) several dodecanuclear manganese complexes with the general composition $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_x]$ ($x=3$ or 4)¹⁻⁵ and their corresponding singly reduced salts $(\text{PPh}_4)[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_x]$,⁶ ii) several distorted Mn_4 cubane molecules with a $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}_3\text{O}_3\text{X}]^{6+}$ core⁷ and iii) tetranuclear vanadium(III) complexes with a butterfly structure⁸. A ferric complex $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]^{8+}$ where tacn is triazacyclononane, has also been reported to display frequency-dependent out-of-phase signals and magnetization hysteresis loops.⁹

The most thoroughly studied family of SMM's are Mn_{12} complexes. Each Mn_{12} molecule has an appreciable potential-energy barrier for reversal of the direction of its magnetization vector. If a sample of the first complex discovered to be a SMM, $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]\cdot\text{S}$ (**1**) where R is CH_3 and S is $2(\text{CH}_3\text{CO}_2\text{H})\cdot 4(\text{H}_2\text{O})$, is magnetized in a strong magnetic field at 2K and the external field is suddenly removed, the magnetization of complex **1** decays to zero with a half life of 2 months.³ Magnetization hysteresis loops and out-of-phase ac magnetic susceptibility signals are also observed due to the slow magnetization relaxation processes that these complexes experience at low temperatures. In addition, complex **1** exhibits steps on its hysteresis loop that are due to quantum tunneling of magnetization tunneling (QTM).¹⁰⁻¹¹

It is important to understand the mechanism(s) by which a SMM changes its direction of magnetization by tunneling through its potential-energy barrier, especially if the potential application of single-molecule magnets to memory devices is to be realized. In this paper we describe the preparation and characterization of new Mn_{12} complexes that give insight into the mechanism of magnetization

relaxation in these fascinating molecules. Several interesting observations correlating different isomeric forms and their slow magnetization relaxation rates are presented.

EXPERIMENTAL SECTION

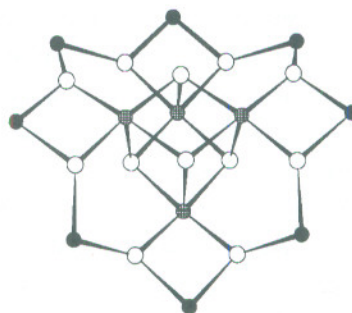
Compound Preparation. Samples of $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$ with different R substituents were prepared by replacing the acetate ligands on complex 1. Complex 1 was synthesized as previously described.¹² A slurry of complex 1 in toluene was treated with an excess (1:32) of the corresponding carboxylic acid RCO_2H . The mixture was stirred overnight in a closed flask and the solution was evaporated until complete dryness. The above treatment was repeated three times. Recrystallization from CH_2Cl_2 /hexanes gave crystals of the various complexes suitable for X-ray structure analyses. All compounds studied gave satisfactory analytical data.

Physical measurements. DC magnetic susceptibility data were collected on microcrystalline samples or a single-crystal sample restrained in eicosane to prevent torquing on a Quantum Design MPMS5 SQUID magnetometer equipped with a 5.5 T (55kOe) magnet. A diamagnetic correction to the observed susceptibilities was applied using Pascal's constants. Alternating current (ac) susceptibility measurements were carried out on a Quantum Design MPMS2 SQUID magnetometer equipped with a 1 T (10kOe) magnet and capable of achieving temperatures of 1.7 to 400 K. The ac field range is $\times 10^{-4}$ to 5 Oe, oscillating at a frequency in the range of 5×10^{-4} to 1512 Hz. Sample alignments in eicosane were performed while keeping the samples in a 5.5 T field at a temperature above the melting point (308-312 K) of eicosane for 15 min., after which the temperature was gradually decreased below the melting point to solidify the eicosane in order to constrain the sample. In this way we could prepare a wax cube with little crystals oriented in the wax cube. Magnetization hysteresis loops were collected on a Quantum Design MPMS5 SQUID magnetometer employing oriented single crystals. The crystals were first added to eicosane and oriented in a 55 kOe field.

ISOMERISM

Complex 1 possess a $[\text{Mn}_{12}(\mu_3\text{-O})_{12}]$ core comprising 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 (see Figure 1). Peripheral ligation is provided by sixteen acetate groups and four H_2O ligands.

FIGURE 1. Drawing of the $[\text{Mn}_{12}\text{O}_{12}]^{16+}$ core showing the relative positions of the Mn^{IV} ions (○), Mn^{III} ions (●) and $\mu_3\text{-O}^{2-}$ bridges (○).



For all the complexes, the eight Mn^{III} ions fall into two groups of four Mn^{III} ions. In group I each Mn^{III} ion is bonded to a single Mn^{IV} via two oxo bridges, while in group II each Mn^{III} is bonded to two Mn^{IV} via two oxo bridges. The four water ligands coordinate only to the four Mn^{III} ions in group II. Assuming that water coordination occurs only at the manganese ions in groups II and only coordinates at the axial positions (up/down) on the Mn^{III} ions, it is possible to identify eleven different geometric isomers. Concomitant rearrangement in the carboxylate ligands is also observed. Of the eleven possible isomeric arrangements of four H_2O ligands, X-ray structures have revealed only four of them. For example, the $\text{Mn}_{12}\text{-Ac}$ (1) has one H_2O ligand on each of the four Mn^{III} ions in group II. For $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_6\text{H}_4\text{-Cl-4})_{16}(\text{H}_2\text{O})_4]$ (2) there are two H_2O ligands on one Mn atom of group II and two H_2O ligands in another Mn atom of the same group. This same "trans" combination of two H_2O /two H_2O ligand positioning was also found for $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_6\text{H}_5)_{16}(\text{H}_2\text{O})_4]$ (3). Special mention is needed for the structure of $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CEt})_{16}(\text{H}_2\text{O})_3]\cdot 4\text{H}_2\text{O}$

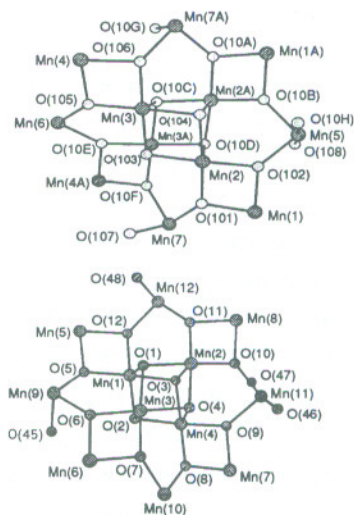
(4). In many respects, the structure of complex 4 is quite similar to those characterized for complexes 1-3. The main difference is that complex 4 has only three bound H_2O ligands, with one of the Mn atoms being five coordinate.

MAGNETISM

High-field magnetization and electron paramagnetic resonance (EPR) have indicated that the ground state of complex 1 is $S=10$. From an oversimplified point of view, this ground state can be understood if we assume that the Mn^{IV} ions ($S=3/2$) of the central $[\text{Mn}^{\text{IV}}_4\text{O}_4]^{8+}$ cubane are aligned with all the spins down that interact ferromagnetically with all the eight Mn^{III} ions ($S=2$) of the external ring that have all spins aligned up. The strong uniaxial magnetic anisotropy has as its origin the single-ion zero field splitting experienced by each Mn^{III} ion. This magnetoanisotropy splits the $S=10$ ground state of the Mn_{12} molecule into $M_s = \pm 10, \pm 9, \dots, \pm 1, 0$ levels. In zero field and if $D < 0$, the $M_s = \pm 10$ levels are the lowest in energy followed by the $\pm 9, \pm 8, \dots, \pm 1$ and 0 levels. As a result, an energy barrier for interconverting the magnetic moment of the molecule from spin "up" to spin "down" occurs and slow magnetization relaxation processes are observed. Indeed, a Mn_{12} complex cooled to a low temperature such that $kT < 100|D|$, exhibits a slow rate of interconversion between spin "up" and spin "down" orientations due to the barrier in the double-well potential-energy curve. When this rate is comparable to the rate of oscillation of the ac field in an ac magnetic susceptibility experiment, there will be a decrease in the in-phase component of the susceptibility, χ_M' , and the appearance of an out-of-phase ac signal χ_M'' . $\text{Mn}_{12}\text{-Ac}$ (1) displays frequency-dependent χ_M'' peaks in the region 4-7K for an ac field oscillating in a range of 50-1000 Hz. Recently, new Mn_{12} molecules have been synthesized that display a peak in the 2-4K region. The observation of two χ_M'' peaks is interesting. It is important to understand the factors that control this phenomenon because the χ_M'' peak positions reflect the rate of

magnetization relaxation. In a previous communication³ we reported that repeated preparations of $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_6\text{H}_4\text{-Me-4})_{16}(\text{H}_2\text{O})_4]\text{S}$ lead to samples that display different ratios of χ_M'' peaks in the 2-4 K and 4-7 K regions. In addition, two different crystallographic forms were characterized.

FIGURE 2 Structure of the cores of the Mn_{12} complexes in (upper) $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_6\text{H}_4\text{-Me-4})_{16}(\text{H}_2\text{O})_4]$ ($\text{HO}_2\text{CC}_6\text{H}_4\text{-Me-4}$) (5), where the O(107), O(108), O(10H) and O(10G) oxygen atoms correspond to the H_2O ligands, and (lower) $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_6\text{H}_4\text{-Me-4})_{16}(\text{H}_2\text{O})_4]3(\text{H}_2\text{O})$ (6), where the O(45), O(46), O(47) and O(48) oxygen atoms correspond to the H_2O ligands



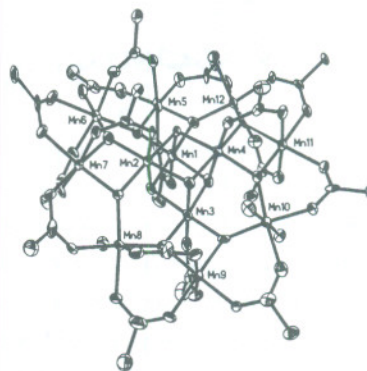
Complex $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_6\text{H}_4\text{-Me-4})_{16}(\text{H}_2\text{O})_4](\text{HO}_2\text{CC}_6\text{H}_4\text{-Me-4})$ (5) shows a frequency-dependent χ_M'' peak in the 2-4K range, while complex $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_6\text{H}_4\text{-Me-4})_{16}(\text{H}_2\text{O})_4]3(\text{H}_2\text{O})$ (6) shows a frequency-dependent χ_M'' peak in the 4-7 K range. This clearly indicates that the relaxation rates for complex 5 is faster than that for complex 6. The main difference between these two Mn_{12} complexes is the relative position of the four H_2O ligands. Complex 5 has a 1,2,1 arrangement of H_2O ligands (one Mn^{III} ion does not have a H_2O ligand), whereas complex 6 has 1,1,2 arrangement.

What is(are) the origin(s) of the two relaxation processes associated with the two different χ_M'' peaks?. One possible reason for the differences in relaxation rates

observed is that these two complexes show different ground states and/or D values thereby leading to a smaller magnetoanisotropy barrier. The different arrangement of H_2O and carboxylate ligands can lead to different magnetic interactions between the Mn ions and therefore different spin ground states. Another possibility is that both complexes relax via different spin-lattice relaxation pathways. Coupling to the phonon bath is crucial. Therefore, different crystallographic forms may affect the observed magnetization relaxation processes.

To better evaluate this possibility for the origin of the two χ_M'' peaks it was important to characterize other Mn_{12} complexes that have different isomeric arrangements of H_2O and carboxylate ligands. Two new SMM's have been characterized: $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{C}_6\text{H}_5)_{16}(\text{H}_2\text{O})_4]$ (7) and $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{Bu}^t)_{16}(\text{H}_2\text{O})_4]$ (8). Their X-ray structures were determined.

FIGURE 3 Structure of the core of the Mn_{12} complex in $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_2\text{C}_6\text{H}_5)_{16}(\text{H}_2\text{O})_4]$ (7), where the O(13), O(14), O(15) and O(16) oxygen atoms correspond to the H_2O ligands



The $[\text{Mn}_{12}\text{O}_{12}]^{16+}$ cores of these two complexes are essentially superimposable on the cores of complexes 1-6 (see Figure 3). It was interesting to find that complexes 7 and 8 also have the 1,2,1 arrangement of $4\text{H}_2\text{O}$ ligands that was found for complex 6. Figure 4 shows the out-of-phase ac susceptibility signals obtained for complexes 7 and 8 at frequencies of 1000, 250 and 50Hz. Complex 7 shows a χ_M'' peak in the 4-7

K region. On the other hand, complex **8** shows predominantly a 2-4 K peak with a smaller peak in the 4-7 K range.

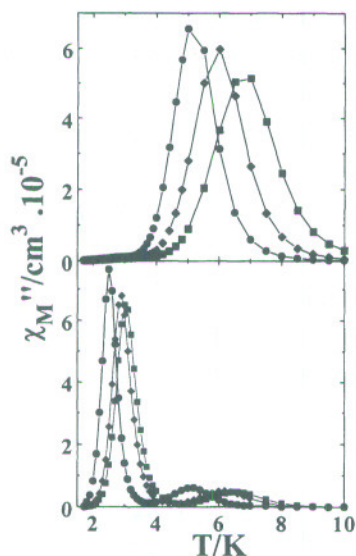


FIGURE 4 Plots of χ_M'' vs. temperature for the p-methylbenzoate complexes **7** (upper) and **8** (lower) in zero dc field and an ac field of 1 G oscillating at 50 Hz (●), 250 Hz (◆) and 1000 Hz (■).

Consequently, changes in the step heights of the magnetization hysteresis loops of complexes **7** and **8** have also been observed. Figure 5 shows magnetization hysteresis loops obtained for oriented crystal samples of complexes **7** and **8**. A few small crystals of a given complex were suspended in eicosane at 40°C, oriented in a 5.5 kG field and then the eicosane matrix was cooled to room temperature. This gives a wax cube with the crystals aligned with their easy axes of magnetization parallel. Steps are seen in the hysteresis loops for both complexes. As can be seen in Figure 5, there are appreciable differences in step heights between complexes **7** and **8**. Complex **8** shows a much steeper step at zero field than does complex **7**. Thus, complex **8** is exhibiting an appreciably faster rate of tunneling of the magnetization than does complex **7**. The greater rate of tunneling for complex **8** is consistent with the fact that this complex shows its χ_M'' signal at a lower temperature than does complex **7**. Thus, it is not simply the isomeric arrangement of 4H₂O and 16 carboxylate ligands that

determines the magnetization relaxation processes in these Mn_{12} complexes. Changes in ground-state S values or the presence of low-lying excited states may be origin of these effects.

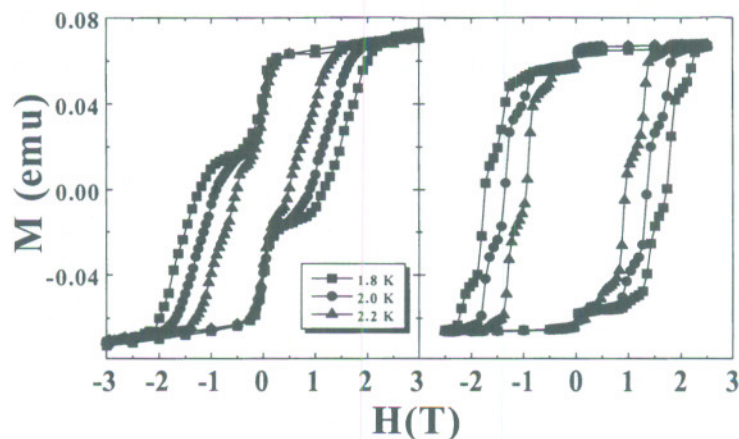


FIGURE 5 Magnetization hysteresis loops measured at different temperatures for oriented crystals in eicosane matrix for complexes 7 (right) and 8 (left).

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