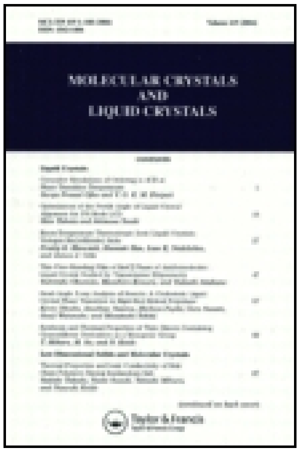

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Single-Molecule Magnets: Magnetization Relaxation and Quantum Tunneling in Dodecanuclear Manganese Complexes

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SINGLE-MOLECULE MAGNETS: MAGNETIZATION RELAXATION AND QUANTUM TUNNELING IN DODECANUCLEAR MANGANESE COMPLEXES

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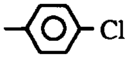
Abstract The syntheses and characterization of three new dodecanuclear manganese complexes with the composition $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ are reported where R is  (**1**),  (**2**), or  (**3**). Complexes **1**-**3** can be prepared with different solvate molecules in the crystal. The X-ray structure of $\mathbf{1}\cdot 8(CH_2Cl_2)$ (**1a**) has been determined. The nature of the solvation influences the out-of-phase AC magnetic susceptibility, χ_M''. Some samples show one χ_M'' peak in the 5-6 K range, others show a χ_M'' peak in the 2-3 K range, and even other compounds show both peaks. These χ_M'' peaks are indicative of a slow relaxation of a single-molecule magnet, where the magnetization of the molecule cannot keep in phase with the oscillating AC magnetic field. Possible explanations for the two χ_M'' peaks are given. Hysteresis loops are seen below ~2.5 K. Step-like features are seen on the hysteresis loops measured for a single crystal of the R = Et (**6**) complex. Quantum mechanical tunneling could be the origin of these step-like features.

INTRODUCTION

There is considerable interest in molecule-based magnets.[1] In one limiting sense of this, molecules are used as the building blocks to build solid structures where, as the result of intermolecular magnetic exchange interactions, domains form consisting of many molecules that lead to magnetic ordering. The other limiting sense is that a single molecule could have a large number of unpaired electrons and enough magnetic anisotropy to function as a single-molecule magnet. In a related active area of research the focus has been on nanoscale magnetic materials.[2] Crystallites of extended magnetic oxides are broken down to such a small size that each microcrystal is a single domain.

Recently molecules have been prepared that have high-spin ground states with large enough magnetic anisotropy to function as single-molecule magnets. Four dodecanuclear manganese complexes, $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ {R = Me (**4**), Ph (**5**) or Et (**6**)} and $(PPh_4)[Mn_{12}O_{12}(O_2CEt)_{16}(H_2O)_4]$ (**7**), have been shown[3-11] to function as single-molecule magnets. Substantiating data comes from several experiments such as hysteresis magnetization loops and out-of-phase AC magnetic susceptibility signals. Very recently a second type of polynuclear manganese complex was reported[12] to exhibit single-molecule magnetic behavior. Distorted-cubane $[Mn^{IV}Mn^{III}_3O_3X]$ (X = Cl or Br) complexes have a $S = 9/2$ ground state with appreciable magnetic anisotropy due to single-ion zero-field interactions.[13] These tetranuclear complexes also exhibit slow magnetization relaxation characteristic of single-molecule magnets.

In this paper we describe the preparation and characterization of three new Mn_{12} complexes. Several interesting observations about the slow magnetization relaxation in the Mn_{12} complexes are presented.

OUT-OF-PHASE AC SUSCEPTIBILITY

In the AC susceptibility experiment the direction of the magnetic field is varied at a known frequency. The magnetic moment of a simple paramagnetic molecule can easily keep in phase with an AC field oscillating in the 25-1000 Hz range. Detailed susceptibility[3] and EPR studies[4] of complex **4** have shown that it has a $S = 10$ ground state experiencing axial zero-field splitting, $(D\hat{S}_z^2)$ where the zero-field parameter $D = -0.50\ cm^{-1}$. Thus, the $S = 10$ ground state is split into $M_s = \pm10, \pm9, \cdots \pm1, 0$ levels. In zero-field there are two states with the same lowest energy value, the $M_s = 10$ and the $M_s = -10$ states. The $M_s = 10$ state could be viewed as the case where the magnetic moment of the Mn_{12} molecule is "up" and the $M_s = -10$ state where the moment is "down". The double well shown in Figure 1 represents the change in potential energy as a given complex converts from spin up to spin down.

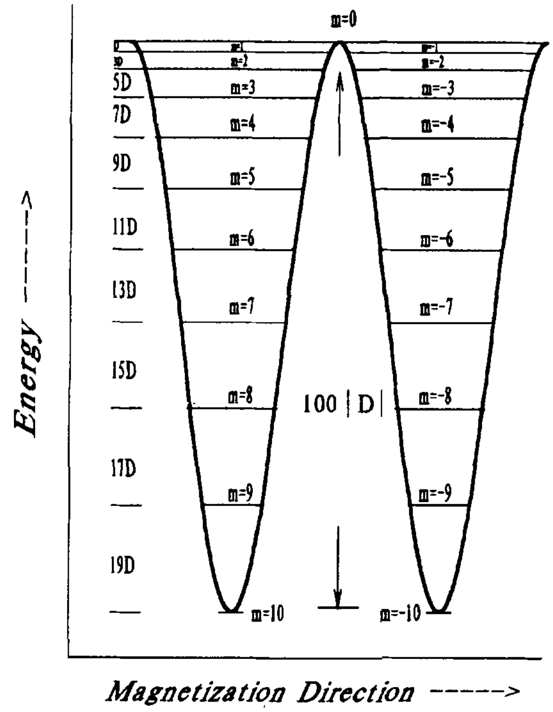


FIGURE 1 Plot of potential energy *vs.* the magnetization direction for a single molecule with a $S = 10$ ground state. Axial zero-field interactions split the $S = 10$ state into ±10, ±9, ····, ±1, 0 levels. The barrier height is 100|D| for the thermally activated process involving converting the magnetic moment of the molecule from the "spin up" $M_S = 10$ level to the "spin down" $M_S = -10$ level.

The barrier is due to zero-field interactions and is of the magnitude 100|D|. A Mn_{12} complex cooled to a low temperature such that $kT < 100|D|$ could exhibit 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, then there will be a drop in the in-phase component of the susceptibility, χ_M', and the appearance of an out-of-phase AC signal χ_M''. These Mn_{12} complexes do show such a sluggish magnetization relaxation as indicated by an χ_M'' AC signal.

Complexes **4**, **5** and **7** have been reported[6,11] to show one χ_M'' AC susceptibility signal. For each complex a single χ_M'' peak is seen at a given frequency of AC field. The temperature of the χ_M'' peak is frequency dependent; each peak shifts to lower temperature with a decrease in AC frequency. In contrast, complex **6** was reported to show two χ_M'' AC peaks. At 499 Hz, for example, one peak is seen at 6.4 K with a second peak at 2.6 K. The latter peak is approximately one-half the intensity of the former. The nature of these two out-of-phase AC signals is one of the focal points of this paper.

Three new Mn_{12} complexes were prepared to investigate the origin of the multiple χ_M'' AC signals. In Figure 2 are plotted the AC susceptibility data taken at three different frequencies for complex $1 \cdot 8(CH_2Cl_2)$, *i.e.*, a solvate with eight methylene chloride molecules. The product of the in-phase AC susceptibility (χ_M') and the temperature is plotted versus temperature. Data are given at three frequencies: (●) 50 Hz; (▼) 250 Hz; and (■) 1000 Hz. The AC field is 1.0 G and the DC field is zero. As the temperature is decreased below ~5-6 K there is an abrupt decrease in χ'_MT. Another decrease occurs below ~2-3 K. These drops in the in-phase signals occur with the appearance of out-of-phase AC signals (lower part of Figure 2). It can be seen that for this solvate of complex **1** there are two χ_M'' AC signals of comparable intensity.

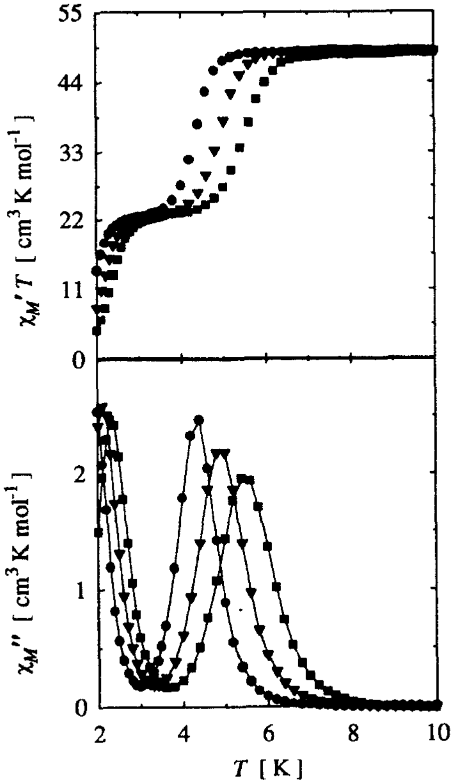


FIGURE 2 AC magnetic susceptibility data for complex $1 \cdot 8(CH_2Cl_2)$.

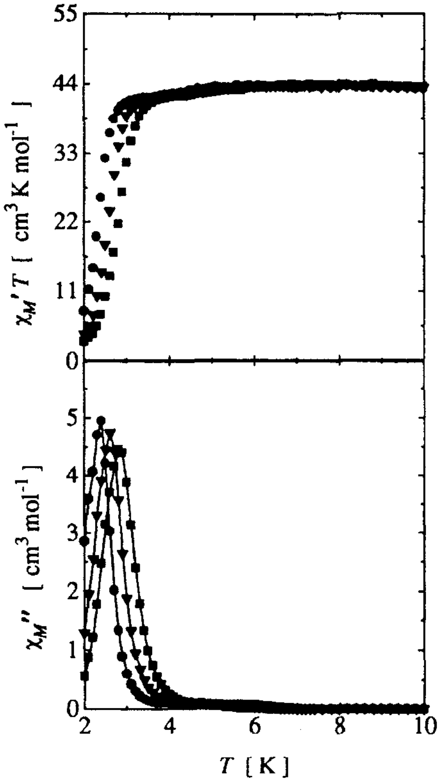
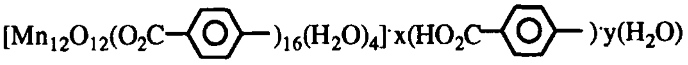


FIGURE 3 AC magnetic susceptibility data for complex $3 \cdot CH_2Cl_2$.

We have found that not only is it possible to prepare Mn_{12} complexes with one χ_M'' AC peak in the 5-6 K range, but complexes can be prepared with two peaks (~2-3 and ~5-6 K) or with only the low-temperature peak at ~2-3 K. In Figure 3 are shown the AC susceptibility data for complex **3**·CH_2Cl_2. The data for this compound were collected at the same three frequencies as used for complex **1**·8(CH_2Cl_2). It can be seen that this complex only shows the low-temperature χ_M'' peak, which occurs at 2.8 K with a 1 G field oscillating at 1000 Hz and shifts to 2.4 K at 50 Hz.

Several experiments were carried out in order to identify the origin of the two out-of-phase AC signals. One major factor affecting whether a given sample shows a 5-6 K peak, a 2-3 K peak or both is the nature of the solvate molecules in the crystal. In Figures 4 and 5 are shown AC susceptibility data collected for two different samples of complex **2**. One sample (called **2a**) analyzed to have three molecules of p-methylbenzoic acid as solvate molecules; the other sample (**2b**) analyzed to have $^1/_2$ molecule of p-methylbenzoic acid and 5 H_2O molecules. In Figure 4 (bottom) it can be seen that sample **2b** shows only one drop off in χ'_MT as the temperature is decreased below ~5-6 K. On the other hand sample **2a** shows one smaller drop off in χ'_MT in the ~5-6 K region, followed by a larger drop off in the ~2-3 K region. These two samples were prepared in the same manner. Both complexes were formed by the reaction of $Mn(ClO_4)_2$ with $(NBu^n{}_4)(MnO_4)$ in ethanol, followed by recrystallization in a solution of CH_2Cl_2 and hexanes. The only difference is that for sample **2a** the ethanol was absolute, whereas in the case of sample **2b** the solution was 80% ethanol, 20% water.

Figure 5 shows that by changing the amount x and y of solvate molecules in  (complex **2**) the appearance of the χ_M'' *versus* temperature plot changes. Sample **2b** (lower plot) essentially only exhibits the ~5-6 K peak, while sample **2a** (top plot) shows dominantly the ~2-3 K peak. Powder X-ray diffraction data run for these two samples indicate that there are two different crystal forms, depending on the crystal solvate molecules.

What is(are) the origin(s) of the two relaxation processes associated with the two different χ_M'' peaks? It should be emphasized that we have studied several different samples prepared for complexes **1**, **2**, and **3**. At a given frequency in the AC susceptibility experiment only one or both of the above mentioned χ_M'' peaks are seen.

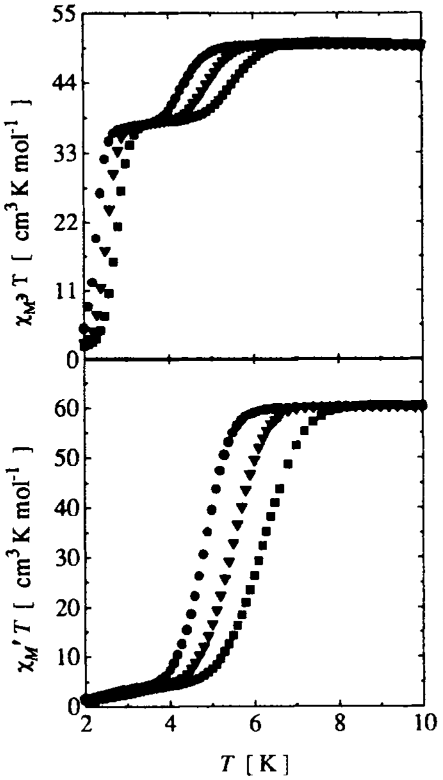


FIGURE 4 Plots of in-phase AC signal χ_M' times temperature *versus* temperature for two different samples of complex **2**.

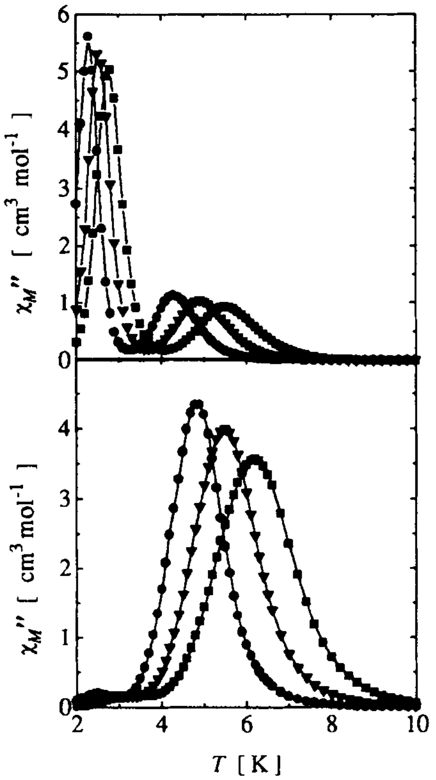


FIGURE 5 Plots of the out-of-phase AC susceptibility *versus* temperature for two different samples of complex **2**.

We have not seen other peaks at temperatures intermediate between the ~5-6 K and ~2-3 K peaks. There does not seem to be distributions of peaks at several different temperatures. In a crystal with solvate molecules there may be defects associated with different amounts of solvate molecules. This could give a distribution of environments about Mn_{12} complexes in a given crystal. This does *not* seem to be the explanation for the peaks in two temperature regions.

If there are indeed different crystallographic forms of a complex depending on the solvate composition, then a possible explanation for χ_M'' AC peaks in two temperature regions comes to mind. In one crystal, the Mn_{12} complex may have a $S = 10$ ground state with $D = -0.50$ cm^{-1}, where D is the axial zero-field interaction parameter. This is the case for complex **4**. In this case, the barrier in Figure 1 is $S^2|D| = 100|D| = 50$ cm^{-1}. In another crystallographic form the ground state may be other than $S = 10$. Some evidence for the solvate composition influencing the spin of the ground state has already been presented.[3] If in the second crystallographic form the Mn_{12} complexes have a different environment and different *intra*molecular magnetic exchange interactions, then there could be a $S = 9$ ground state. Furthermore, if the $S = 9$ complexes have $D = -0.40\ cm^{-1}$, then the potential-energy barrier is $S^2|D| = 81\ (0.40\ cm^{-1}) = 32.4\ cm^{-1}$. This is approximately one half the barrier for the $S = 10$ molecules. Such a reduction in barrier height would cause a shift to a lower value of the temperature at which the χ_M'' AC signal is seen.

There are, of course, other possible explanations for the origin of the two relaxation processes seen in the χ_M'' *versus* temperature plots. The ~5-6 K peak could be associated with an individual molecule converting between the two minima on its double-well potential-energy curve (Figure 1). The ~2-3 K peak could be associated with a cooperative event in the crystal, such as phase transition to a magnetically ordered state of the whole crystal. The frequency dependence of the ~2-3 K peak for all complexes and the absence[14] of any thermal anomalies in the heat capacity data for complex **4** do not support the presence of such a phase transition.

X-RAY STRUCTURE OF COMPLEX 1

The single-crystal X-ray structure of **1**·8(CH_2Cl_2) was determined to see if there was any evidence why this complex exhibits two χ_M'' AC peaks. Crystals were grown from a CH_2Cl_2 solution. In order to prevent loss of the 8(CH_2Cl_2) solvate molecules it was necessary to remove a crystal from the solution and immediately stick it in silicone and cool it to 101 K. It was found that the $[Mn_{12}O_{12}(O_2CC_6H_4Cl)_{16}(H_2O)_4]$ complex is located on a crystallographic two-fold axis in the space group C2/c. Two of the Mn atoms are located on the two-fold axis. The unit cell was characterized to have a = 29.697(9) Å, b = 17.708(4) Å, c = 30.204(8) Å with Z = 4. The structure was solved and the final R_F is 10.9%. In addition to one half of the Mn_{12}-complex the asymmetric unit was found to contain eight partially occupied molecules of CH_2Cl_2. Two of the p-chlorobenzoate ligands were found to be disordered (50% in 2 positions).

The X-ray structure of complex **1**·8(CH_2Cl_2) shows a Mn_{12} complex that is very similar to those found[6] in complexes **4**, **5** and **6**. All four H_2O ligands sites are fully occupied in **1**·8(CH_2Cl_2). The only features that are somewhat different are the two disordered p-chlorobenzoate ligands.

It must be emphasized that a portion of the same crystalline sample from which the above single crystal was taken was used to run the AC susceptibility data shown in

Figure 2. Thus, the X-ray structure did *not* reveal any cause for the two χ_M'' AC signals seen for complex **1**.

HYSTERESIS LOOPS

If a molecule functions as a single-molecule magnet, then there should be hysteresis effects present. The existence of a hysteresis loop in the response of magnetization to an external magnetic field is, of course, a reflection of the presence of some kinetic process. For ferromagnets or ferroelectrics, for example, the presence of domain structure is required to give hysteresis. As the magnetic field is increased, the domains with moments misaligned with the field are consumed by the domains with their moments favorably aligned. It is the kinetics associated with the domain wall (boundaries between aligned regions) movement that dictate whether a hysteresis loop is seen and the shape of the loop. It has already been established[3,5,6] that these Mn_{12} complexes exhibit magnetization hysteresis loops. In contrast to ferromagnets or ferroelectrics, the magnetization hysteresis loop observed for a Mn_{12} complex is due to a single molecule interacting with the magnetic field.

Magnetization hysteresis loops have been reported[3,5,6] for Mn_{12} complexes **4**, **5** and **6**. Paulsen *et al.*[8] examined the hysteresis characteristics of complex **4** in detail. A bundle of five single crystals (~6 mg) was oriented and studied in a SQUID equipped with a 8T magnet and a dilution refrigerator capable of reaching 100 mK. Hysteresis curves were studied from 3.25 K down to 180 mK, employing a field sweeping rate of ~10 kG/h. At temperatures below ~1.5 K they saw step-like features in the hysteresis loops. The origin of the so-called "avalanche" phenomenon was unclear.

To further establish the origin of the "avalanche" phenomenon manifested in the Mn_{12} system we have investigated the low temperature hysteric behavior of one needle shaped single crystal (<0.1 mg) of complex **6**. The crystal was oriented so that the long axis of the needle was parallel to the direction of the external field. The angle between the needle axis and the z-axis of the molecule was determined to be 52°. In contrast to previous measurements on polycrystalline and ensembles of crystals these measurements of an individual, isolated crystal will facilitate a more straightforward characterization of the "avalanche" phenomenon while eliminating spurious effects resulting from variations in the crystal sizes and interparticle interactions. Hysteresis loops for the needle crystal were obtained using a Quantum Design MPMS-7T SQUID magnetometer equipped with a recently developed reciprocating sample option (RSO). The RSO is based on a technique that employs small-amplitude oscillations of the sample inside the SQUID magnetometer's second order gradiometer. The periodic movement produces an AC signal that is detected by the SQUID sensor. Synchronous detection of the sample signal by digital AC electronics make the RSO measurements

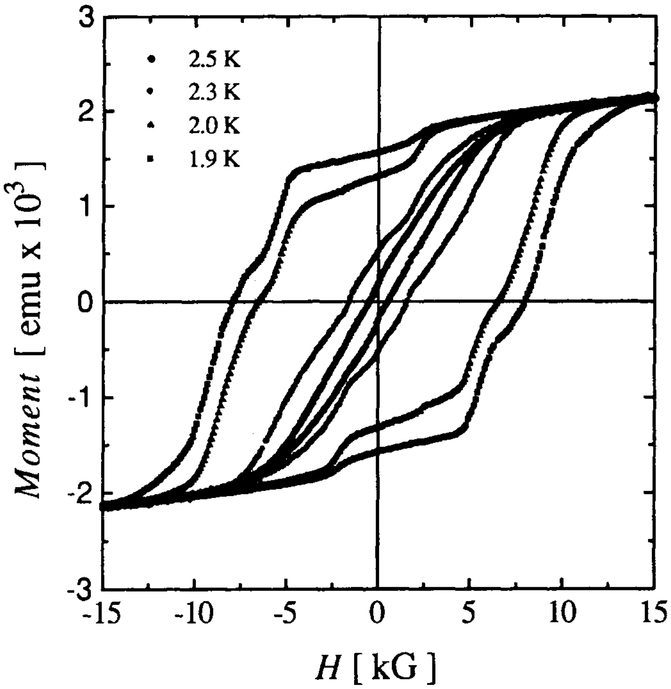


FIGURE 6 Hysteresis loops for a single crystal of $[Mn_{12}O_{12}(O_2CEt)_{16}(H_2O)_3]\cdot H_2O$ (**6**).

less susceptible to environmental magnetic and SQUID drifts resulting in a greater differential sensitivity than traditional SQUID magnetometers.

Figure 6 presents the hysteresis loops collected in 100 G increment steps for the needle single crystal over the 1.9-2.5 K temperature range. The experiments were performed by charging the superconducting magnet to a specific current, and then operating it during the measurements in a persistent mode eliminating the noise commonly associated with current sources and power supplies. The data shows distinct step-like features in the hysteresis loops for the complex **6**. As the resolution of the steps improves with decreasing temperatures these experiments required thermal stability over long periods of time [typically ~20 hr for each M(H) curve] at the lowest temperatures reached by the instrument. A continuous low temperature control mode of the magnetometer was employed for the first time to allow extended temperature operation below 4.2 K. The measurements showed that the number of steps increase with decreasing temperature. A quantitative analysis of the spacing between the steps is currently in progress to further establish the underlying mechanisms responsible for this phenomenon.

The exact origin of the step-like features in the hysteresis loops for complex **6** is not known. One possible origin can be suggested by reference to Figure 1. If a crystal of a Mn_{12} complex is oriented such that the magnetic z axis of each Mn_{12} molecule is parallel to the direction of an external magnetic field, then the potential-energy curve shown in Figure 1 is appropriate. This curve is drawn for zero magnetic field and shows the zero-field split quantized states for one Mn_{12} complex on either side of the potential-energy barrier. If a large saturating magnetic field is applied to the single crystal, the $M_s = -10$ state would be greatly stabilized in energy relative to the $M_s = 10$, *i.e.*, one minimum of the double well is stabilized relative to the other. If the crystal was kept at very low temperatures in a saturating field, all of the Mn_{12} complexes would be in the $M_s = -10$ state. If the magnetic field could be suddenly reduced to zero, then the population of molecules would change to have 50% in the $M_s = -10$ state and 50% in the $M_s = 10$ state.

In running the 1.9 K hysteresis loop shown in Figure 6, the field is gradually decreased from 15.0 kG. It can be seen that at a field of 2.1 kG then at fields of -5.6 and -9.1 kG there are steps where the magnetization decreases more rapidly. It is possible that these surges in rate of decrease in magnetization reflect alignment of states between the two halves of the double well. That is, whenever a $M_s = -n$ state of the right half of the double well has the same energy as a $M_s = +m$ state of the left half of the double well, there could be a surge in molecules converting due to enhanced quantum mechanical tunneling. The intervals between the steps would relate to the energy differences between states in the double well.

The concept of quantum mechanical tunneling of magnetization, *i.e.*, domain walls, has been the focus of recent research dealing with nanoscale magnets. It would be fascinating if the steps observed in the hysteresis loops for complex **6** were indeed due to tunneling. Very recently there have been papers[15,16] from two groups reporting the presence of regularly spaced steps on the magnetization hysteresis loops for a crystal of $[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4]{\cdot}2(CH_3CO_2H){\cdot}4(H_2O)$. Upon decreasing the magnetic field the first step was observed at zero field. The steps occur at regular intervals and agree with the magnitude of zero-field splitting in the $S = 10$ ground state of this acetate complex. At this time it is not clear why the first step we observe for the single crystal of complex **6** occurs at ~2,100 G, not zero field.

The Mn_{12} complexes have integer-spin ground states with S = 10 or 9. Quantum mechanical tunneling between the zero-field split levels of an integer-spin ground-state molecule is quantum mechanically allowed.[17] On the other hand, quantum tunneling between the levels of an half-integer ground-state molecule are not allowed. It will be interesting to determine whether step-like features are seen on the hysteresis loop of $(PPh_4)[Mn_{12}O_{12}(O_2CEt)_{16}(H_2O)_4]$ (**7**). The $[Mn_{12}O_{12}(O_2CEt)_{16}]^-$ anion in this complex has a half-integer ground state,[6] with $S = {}^{19}/_2$.

ACKNOWLEDGMENTS

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