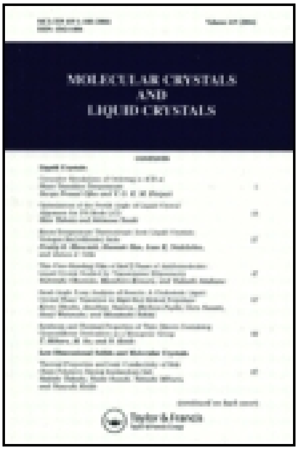

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Single-Molecule Magnets

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Single-Molecule Magnets

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Metal cluster complexes with interesting magnetic properties characteristic of nanoscale magnetic particles have become an attractive prospect in the last few years. These complexes exhibit magnetization hysteresis loops and out-of-phase ac magnetic susceptibility signals. The advantages of such clusters over fragmented bulk ferromagnets are their easy synthesis and manipulation, their high solubility, and their potential use in storing a large density of information. Here we will focus our attention on the family of several distorted Mn_4 cubane molecules with a $[Mn^{IV}Mn^{III}{}_3O_3X]^{6+}$ core, tetranuclear vanadium(III) complexes with a butterfly structure and dodecanuclear manganese complexes, $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ (where R can be an aliphatic or aromatic group) and their corresponding singly reduced salts $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4](PPh_4)$, which have been extensively studied in our laboratories.

Keywords: clusters; single-molecule; magnets; hysteresis

INTRODUCTION

Large metal cluster complexes with interesting magnetic properties characteristic of nanoscale magnetic particles, such as magnetization hysteresis loops and out-of-phase ac magnetic susceptibility signals, have been synthesized. The discovery of these unexpected magnetic properties in metal cluster chemistry represented an exciting breakthrough for a number of reasons: 1) metal clusters are normally prepared by a solution method and, once purified, are composed of 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 sub-nanoscale dimensions, such materials could potentially be used for storing a large density of information; and 5) from a theoretical point of view, understanding the magnetic properties of these molecules is important to help bridge the gap between the quantum and classical understanding of magnetism.[1]

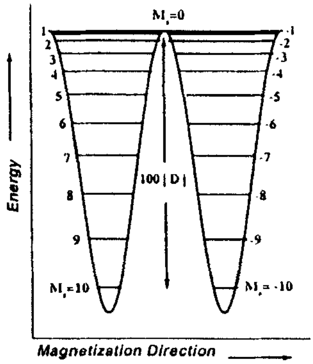
In 1993 it was discovered that $[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4].4H_2O.2CH_3CO_2H$ (1) (complex **1** or $Mn_{12}Ac$ for short), functions as a nanoscale magnet.[2,8] Such a molecule has been termed a single-molecule magnet (SMM). Since then, a few more families of complexes that function as SMM's have been obtained: 1) several other structurally related dodecanuclear manganese complexes, $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ where R can be an aliphatic or aromatic group, and their corresponding singly reduced salts $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4](PPh_4)$;[3-13] 2) several distorted Mn_4 cubane molecules with a $[Mn^{IV}Mn^{III}{}_3O_3X]^{6+}$ core[14] , 3) a mixed-valent $[Mn_4(O_2CMe)_2(Hpdm)_6][ClO_4]_2$[15], 4) tetranuclear vanadium(III) complexes with a butterfly structure[16], and 5) a ferric complex $[Fe_8O_2(OH)_{12}(tacn)_6]^{8+}$, where tacn is triazacyclononane, which has been reported to display frequency-dependent out-of-phase peaks and magnetization hysteresis loops.[17] In this paper we report the series of families 1-4, which have been extensively studied in our laboratories.

ORIGIN OF THE SINGLE-MOLECULE MAGNETISM

Magnetization relaxation data on frozen solutions or polymer-doped samples and the lack of any anomaly in heat capacity measurements collected in zero-field confirmed that the slow magnetization relaxation rates exhibited by these complexes are due to individual molecules rather than to long range ordering as is commonly observed in nanoscale magnetic domains.[18] The single-molecule magnetism behavior observed for the clusters shown in this paper originates from a combination of a large-spin ground state and a negative magnetoanisotropy. For instance, in the case of complex **1** high-field magnetization and electron paramagnetic resonance (EPR) studies have indicated that this complex has a high-spin ground state with

S=10.[6] From a simplified point of view, this ground state can be understood if we assume that the four Mn^{IV} (S=3/2) ions of the central $[Mn^{IV}_4O_4]^{8+}$ cubane are aligned with all the spins down and they interact antiferromagnetically with the eight Mn^{III} (S=2) ions of the external ring that have all spin aligned up. The strong uniaxial magnetic anisotropy of the molecule originates from the single-ion zero field splitting experienced by the Mn^{III} ions. This zero-field interaction splits the S=10 ground state into the different m_s= ±10, ±9, ±8, ±7........0 levels (see Figure 1).

FIGURE 1. Plot of potential energy *vs.* the magnetization direction for a single molecule with an S=10 ground state split by axial zero-field splitting.



In zero field, the m_s=±10 levels are the lowest in energy followed by ±9, ±8, ±7,...levels at higher energies and m_s =0 level is at the highest energy. The negative magnetoanisotropy leads to a potential-energy barrier between the spin "up" (i.e., m_s=-10) and spin "down" (i.e., m_s=+10) orientations of the magnetic moment of an individual Mn_{12} molecule. In order for a Mn_{12} SMM to flip spin from "up" to "down", it has to either go over the barrier or it can tunnel through the barrier.

The barrier height is determined by the ground-state spin and the magnetoanisotropy in the ground state.

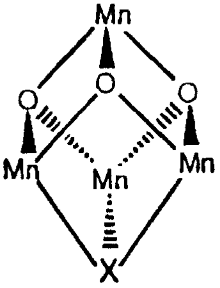
There are different experimental manifestations of the fact that a molecule is functioning as a single-molecule magnet. Two of the more characteristic manifestations are: 1) the observation of frequency-dependent out-of-phase ac magnetic susceptibility signals; and 2) the observation of a hysteresis loop in the magnetization versus external magnetic field response.

MAGNETIC PROPERTIES

Ac susceptibility data were collected on polycrystalline samples of the vanadium complexes $[V_4O_2(O_2CEt)_7(bpy)_2](ClO_4)$(**2**) and $(NEt_4)[V_4O_2(O_2CEt)_7(pic)_2]$(**3**). The core of these complexes contains a $[V_4(\mu_3\text{-}O)_2]^{8+}$ cation comprising four V^{III} ions with a "butterfly" disposition and a μ_3-O^{2-} ion bridging each V_3 "wing".[16] Both complexes exhibit out-of-phase χ_M'' signals although their intensities were rather weak. For complexes **2** and **3**, fitting of dc magnetization *vs.* field data gave an $S=3$ ground state and a negative D value of ~ -1.5 cm^{-1}. Therefore, the barrier to magnetisation reversal from $M_s = -3$ to $M_s = +3$ is $|9D| \approx 13.5$ cm^{-1}, a relatively small number that rationalizes only a weak out-of-phase ($\chi''T$) signal at 1.7 K.

The distorted-cubane Mn_4 complexes reported to exhibit single-molecule magnetism are: $[Mn_4O_3Cl_4(O_2CMe)_3(py)_3]$(**4**), $[Mn_4O_3Cl(O_2CMe)_3(dbm)_3]$(**5**), $[Mn_4O_3F(O_2CMe)_3(dbm)_3]$(**6**), $[Mn_4O_3(N_3)(O_2CMe)_3(dbm)_3]$(**7**), $[Mn_4O_3(NCO)(O_2CMe)_3(dbm)_3]$(**8**), $[Mn_4O_3(OC(O)Me)(O_2CMe)_3(dbm)_3]$(**9**). All these complexes have been reported to have a S=9/2 ground state with axial ZFS such that D=-0.3 cm^{-1}.[14]

FIGURE 2. Scheme of the central distorted cubane $[Mn_4(\mu_3\text{-}O)_3((\mu_3\text{-}X)]^{6+}$ core present in each of the Mn_4 complexes **4**-**9**.



The S=9/2 ground state is split into ±9/2, ±7/2, ±5/2, ±3/2, and ±1/2 levels leading to a $20|D|$ barrier between the spin-up (M_s=+9/2) and spin-down (M_s=-9/2) states. As a consequence, complexes **4**-**9** exhibited frequency-dependent out-of-phase signals in the 1.7-2.0 K region for an ac field oscillating at frequencies between 250 and 1000 Hz. Evidence for field-tuned resonant magnetization tunneling was found in both the dc magnetization hysteresis loops and the ac susceptibility data for complex **5**.[14] More recently,[15] a new mixed-valent $[Mn_4(O_2C\text{-}Me)_2(Hpdm)_6][ClO_4]_2$ (**10**) was reported to have S = 8, g = 1.85 and D = -0.25(3) cm^{-1}. AC susceptibility measurements showed strong out-of-phase χ_M'', with a peak evident at *ca.* 2 K at a 1000 Hz ac frequency.

In the case of complex $Mn_{12}Ac$ (1), frequency-dependent out-of-phase signals in the 4-7 K region for an ac field oscillating at frequencies between 50-1000 Hz were observed. Moreover, for an aligned microcrystalline sample of complex 1 along the z-axis, steps at a constant interval of field in the magnetization hysteresis loops, collected in the temperature region of 1.8-2.6 K, were also observed (see Figure 3).This fact is an indication that in addition to thermal activation of each SMM over the barrier, the reversal of the direction of the magnetization also occurs via quantum mechanical tunneling through the barrier.[19-20] In fact, it has been established that the magnetic relaxation of complex 1 does not follow a classical thermal process climbing over the barrier to convert from the spin "up" to spin "down" but a mixed quantum-thermal process occurs.[21]

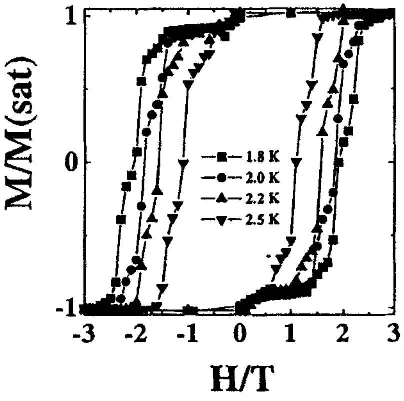
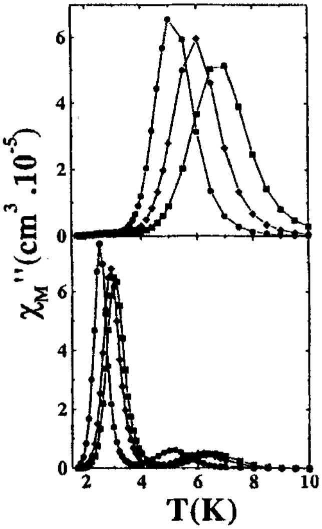


FIGURE 3. Plot of the magnetization hysteresis loop measured at different temperatures for complex 1 oriented in an eicosane wax matrix.

More recently[6-10], an examination of the magnetic properties of new members of the Mn_{12} family showed that not a simple but rather a combination of different magnetization relaxation processes occurs. For example, complex **1** and $[Mn_{12}O_{12}(O_2CCH_2C_6H_5)_{16}(H_2O)_4]$ (**11**) have been reported to show only one χ_M'' ac susceptibility peak in the temperature region of 4-7K.[10] In contrast, complex $[Mn_{12}O_{12}(O_2CC_6H_4Bu^t)_{16}(H_2O)_4].CH_2Cl_2$ (**12**).[10] was reported to exhibit predominantly an out-of-phase ac magnetic susceptibility peak in the temperature region of 2-4 K.[7] The out-of-phase χ_M'' signals of complexes **11** and **12** are shown in Figure 4.

FIGURE 4. Plots of χ_M'' vs. temperature for the complexes **11** (upper) and **12** (lower) in zero dc field and an ac field of 1 G oscillating at 50 Hz (●), 250 Hz (♦) and 1000 Hz(■).



Recently, we found that the molecular origin of the differing magnetic behavior is due to the existence of isomeric forms of the $[Mn_{12}O_{12}]$

core involving different relative orientations of Mn^{III} Jahn–Teller distortion axes. We have termed this new effect 'Jahn–Teller isomerism'.[22]

When the neutral Mn_{12} molecule with an S=10 ground state is reduced by one electron, the spin of the ground state of the anionic complex becomes a half-integer value such as S=19/2. This has been confirmed by high-field EPR spectra that also give an accurate value for the zero-field splitting parameter D=-0.61 cm^{-1}.[11-12] In the case of complexes $(Ph_4P)[Mn_{12}O_{12}(O_2CEt)_{16}(H_2O)_4]$ (**13**) and $(Ph_4P)[Mn_{12}O_{12}(O_2CPh)_{16}(H_2O)_4]$ (**14**) frequency-dependent out-of-phase signals in the 3-5 K region for an ac field oscillating at frequencies between 50-1000 Hz were also observed.

In Figure 5 is shown the magnetization hysteresis loop taken at 1.85 K for an oriented-crystal sample of complex **13**, where steps can clearly be seen. In the lower part of Figure 5 is shown the first derivative of the hysteresis plot. As the field is decreased from +2.0 T the first step is seen at zero field, followed by steps at -0.5, -0.9 and -1.3 T. The steps correspond to increases in the rate of change of the magnetization and are due to resonant tunneling between quantum spin states. This S=19/2 complex tunnels not only at various increments of field but also when H=0 although there have been several papers addressing the fact that a molecule with an half-integer ground state, such as S=19/2, should not exhibit resonant tunneling in the absence of a magnetic field.[19-21]

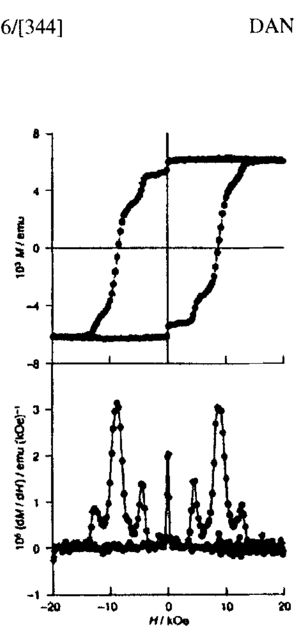


FIGURE 5. The top plot shows the magnetization hysteresis loop measured at 1.85 K for five crystals of $(PPh_4)[Mn_{12}O_{12}(O_2CEt)_{16}(H_2O)_4]$(**13**) oriented in an eicosane wax matrix. In the lower plot is shown a plot of the first derivative of the magnetization hysteresis loop

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