Half-Integer-Spin Small Molecule Magnet Exhibiting Resonant Magnetization Tunneling

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Nanoscale magnets and the unusual properties they are expected to show are an extremely topical area.[1−19] There are, at least, two major reasons for studying nanoscale magnets: the search for a small memory device (molecular computer) and the elucidation of how quantum-mechanical behavior at the microscopic scale underlies classical behavior at the macroscopic scale. Fabrication techniques include fragmenting bulk magnets or building up molecules. Friedman et al.[20] recently reported the first case of a macroscopic measurement of resonant magnetization tunneling in a single-molecule magnet, $[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4]$ (**1**). They observed steps at regular intervals of magnetic field in the magnetization hysteresis loop of oriented crystals of complex **1**. This macroscopic measurement of a molecular tunneling event has been verified by others.[21,22] Here we report the observation of resonant magnetization tunneling for a second single-molecule magnet, $[Mn_4O_3Cl(O_2CCH_3)_3(dbm)_3]$ (**2**), where dbm^- is the anion of dibenzoylmethane. Magnetization tunneling for complex **2** is of particular interest because this Mn_4 molecule has a half-integer-spin $S = {}^9/_2$ ground state and it is appreciably smaller in size than the Mn_{12} molecule.

Each molecule in a crystal of **2** is oriented in the same direction and has a distorted-cubane $[Mn_4(\mu_3\text{-}O)_3(\mu_3\text{-}Cl)]^{6+}$ core.[23] In previous work,[23−25] it has been established that complex **2** and several analogous complexes have a $S = {}^9/_2$ ground state. In contrast to the Mn_{12} complex **1**, the $S = {}^9/_2$ ground state of complex **2** is well isolated, which means that the lowest-lying spin state is $>180\ cm^{-1}$ at higher energy. In a very recent paper[26] we showed that complex **2** and other $Mn^{IV}Mn^{III}_3$ complexes function as single-molecule magnets. Frequency-dependent out-of-phase ac magnetic susceptibility signals were seen for polycrystalline samples at ∼2 K. Similar ac susceptibility data were also obtained for a frozen toluene solution of **2** and this confirms that the out-of-phase ac signal is associated with isolated molecules.

In the present study magnetization data were obtained for a platelike ∼1 × 1 × 0.1 mm single crystal of complex **2** at five different temperatures between 0.426 and 2.21 K employing a Faraday magnetometer equipped with a ^{3}He refrigerator. The single crystal was oriented and fixed in a solid eicosane cube with the external field parallel to the magnetization easy axis of the crystal. After saturation (+2.0 T) the field was cycled between +2.0 T and −2.0 T and back to +2.0 T. No hysteresis loop was seen at 2.21 K. The data at the other four temperatures are shown in Figure 1. Steps are clearly seen in these hysteresis loops. At 0.426 K, as the field is decreased from 2.0 T to −2.0 T, a large step is seen at zero field, with a less pronounced step seen at −0.55 T.

The steps in each hysteresis loop correspond to increases in the rate of change of the magnetization at these fields. The steps are attributable to resonant tunneling between quantum levels. The double-well potential energy diagram for this $S = {}^9/_2$ molecule in zero field is shown in Figure 2. Saturation in a +2.0 T field leads to a stabilization in energy of the $m_s = -{}^9/_2$ state and a destabilization of the $m_s = +{}^9/_2$ state. As the field is cycled from +2.0 T to −2.0 T and back, resonant tunneling occurs because the energy levels in the right-hand part of the double well have the same energies as the levels in the left-hand part of the double well. The spacings between the steps seen in the hysteresis loop are given by $\Delta H = -D/g\mu_B$, where g is the EPR g-factor and μ_B is the Bohr magneton. The parameter D gauges the magnitude of axial zero-field splitting ($D\hat{S}_z^2$) present in the $S = {}^9/_2$ ground state of complex **2**. From the first-derivative plot in Figure 1, the average field interval between steps is calculated to be $\Delta H = 0.55$ T. This gives a value of $D/g = -0.25\ cm^{-1}$, which is consistent with the $D/g = -0.18\ cm^{-1}$ obtained for this compound by fitting variable-field magnetization data[26] and also with fitting of high-field EPR data ($D/g = -0.25\ cm^{-1}$).[27]

Rates of magnetization relaxation for complex **2** have been determined in the 1.7−2.1 K range by means of ac susceptibility measurements and in the 0.394−0.706 K range with the Faraday magnetometer. In the case of the ac susceptibility experiment the frequency of the ac field is held fixed. The frequency of the ac field corresponds to the rate of magnetization relaxation at the temperature at which there is a maximum in the out-of-phase ac signal. In the low temperature range rates of magnetization

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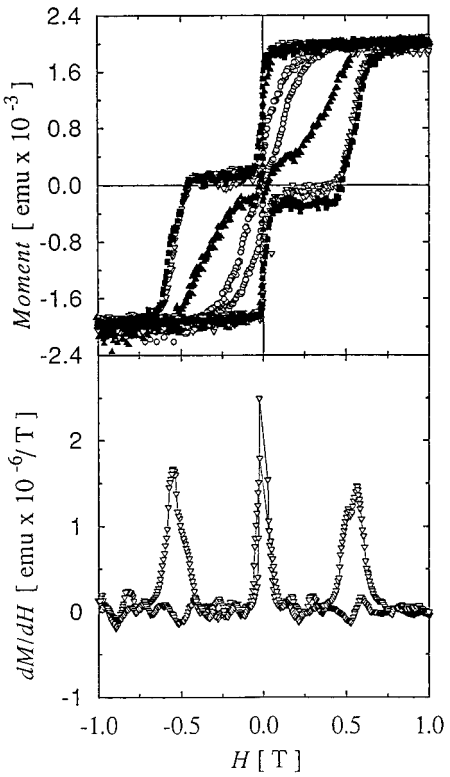

Figure 1. In the top figure are magnetization hysteresis loops measured for a single crystal of $[Mn_4O_3Cl(O_2CCH_3)_3(dbm)_3]$ (**2**) at the following temperatures: (■) 0.426 K; (▽) 0.53 K; (▲) 0.706 K; and (○) 0.90 K with a Faraday magnetometer. In a 5.5 G field, the crystal was oriented in molten eicosane at 30−35 °C and then was cooled to room temperature to give a solid wax cube. The external field was applied parallel to the magnetization easy axis of the crystal. One complete hysteresis loop took 48 min and was measured in the range of 2.0 to −2.0 T. In the bottom figure, the first derivative of the smoothed magnetization curves measured at 0.53 K is shown. The magnetic fields at which steps in the magnetization curves occur are visible in the first-derivative plots.

were determined by saturating the magnetization of a single crystal in the Faraday balance. After the field was rapidly decreased to zero, the decay of the magnetization for the crystal was measured as a function of time. These relaxation data were fit as an exponential decay to give the relaxation rate of each temperature in the 0.394−0.706 K range. An Arrhenius plot of ln(rate) vs. $1/T$ shows an activated higher temperature region with a barrier of ∼12 K and a preexponential factor of 4×10^{-7} s. At the lowest temperature (<0.706 K), the relaxation rate becomes independent of temperature with a tunneling rate equal to 3×10^{-2} s^{-1}.

Resonant magnetization tunneling is also in evidence in the dc field dependence of the ac susceptibility response for complex **2** (Figure 3). With the ac field held at an amplitude of 1.0 G and oscillating at 1000 Hz there is a field dependence in the temperature at which a maximum in the out-of-phase ac signal is seen. A peak occurs when the relaxation rate of the molecule matches the frequency of the ac measuring field. If only a thermally activated process is responsible for the slow relaxation, as the dc field is increased a monotonic decrease in peak temperature would result since the barrier height is decreasing. However, the plot of peak temperature vs. H (Figure 3) shows two minima: one at zero field and the other at −0.59 T. These are the fields corresponding to resonant tunneling.

The very large step seen in the hysteresis loop when crossing zero field is fascinating. In contrast to the even-spin ($S = 10$) Mn_{12} complex **1**, a molecule with a half-integer ground state such as $S = {}^9/_2$ should not exhibit resonant tunneling in the absence of a magnetic field.[28,29] The $m_s = \pm{}^9/_2$ states comprise a Kramers

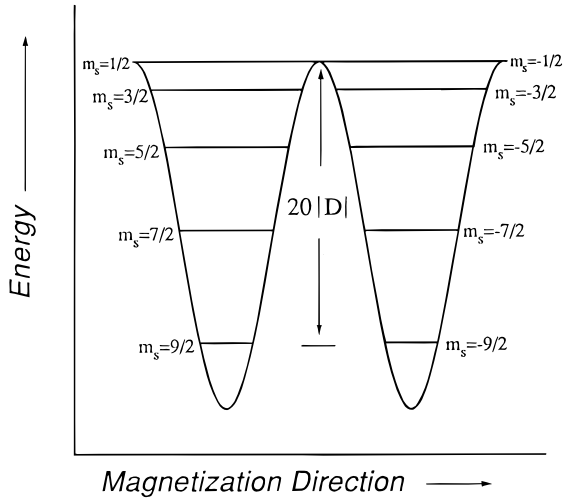

Figure 2. Plot of the potential energy versus the magnetization direction for a single molecule with a $S = {}^9/_2$ ground state in the absence of a magnetic field. Axial zero-field interactions split the $S = {}^9/_2$ state into $m_s = \pm{}^9/_2, \pm{}^7/_2, \pm{}^5/_2, \pm{}^3/_2$, and $\pm{}^1/_2$ levels. The barrier height U is equal to $20|D|$ for the thermally activated process involving converting the magnetic moment of the Mn_4 molecule from the "spin up" $m_s = {}^9/_2$ level to the "spin down" $m_s = -{}^9/_2$ level. The value of D gauges the axial zero-field splitting (spin Hamiltonian $H = D\hat{S}_z^2$) in the ground state. Physically, the zero-field splitting in the ground state has as its origin single-ion zero-field interactions at each of the Mn^{III} ions in the Mn_4 molecule.

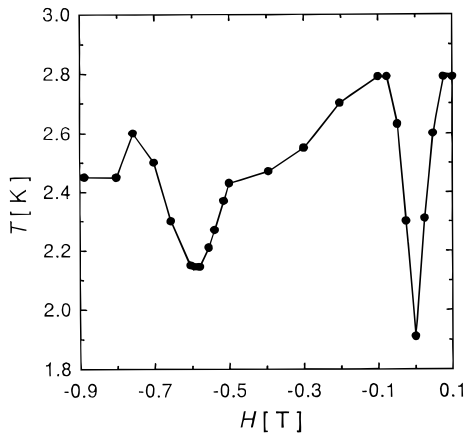

Figure 3. Plot of the temperature at which a maximum in the out-of-phase ac susceptibility signal occurs as a function of external magnetic field for Mn_4 complex **2**. The sample consisted of several crystals (14.4 mg) of complex **2** oriented by an external field in eicosane that was cooled to give a solid cube. The 1000 Hz field had an amplitude of 1.0 G. The dc field was parallel to the easy axis of the oriented single crystals. At each setting the ac susceptibility was determined in the 1.7−10 K range.

degenerate pair in zero field. Thus, a $S = {}^9/_2$ molecule should not be able to tunnel *coherently* between the $m_s = -{}^9/_2$ and $m_s = +{}^9/_2$ levels. There is a small internal magnetic field established by the nuclear spins of the Mn ions ($I = {}^5/_2$) and the protons ($I = {}^1/_2$). A transverse component of such a nuclear-spin magnetic field may lead to resonant tunneling for an oriented collection of Mn_4 molecules in zero external field.

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