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 macroscopic 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, \([\text{Mn}_{4}\text{O}_3\text{Cl(O}_2\text{CCH}_3\text{)}_3\text{dbm}]{_3}\) (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, \([\text{Mn}_{4}\text{O}_3\text{Cl(O}_2\text{CCH}_3\text{)}_3\text{dbm}]{_3}\) (2), where dbm– is the anion of dibenzoylmethane. Magnetization tunneling for complex 2 is of particular interest because this Mn4 molecule has a half-integer-spin \(S = \frac{7}{2}\) ground state and it is appreciably smaller in size than the Mn2 molecule.

Each molecule in a crystal of 2 is oriented in the same direction and has a distorted-cubane \([\text{Mn}_4(\mu_4-\text{O})_3(\mu_4-\text{Cl})]^{6+}\) core.23 In previous work,23-25 it has been established that complex 2 and several analogous complexes have a \(S = \frac{7}{2}\) ground state. In contrast to the Mn2 complex 1, the \(S = \frac{7}{2}\) ground state of complex 2 is well isolated, which means that the lowest-lying spin state is \(\sim 180 \text{ cm}^{-1}\) at higher energy. In a very recent paper26 we showed that complex 2 and other MnIVMnIII complexes function as single-molecule magnets. Frequency-dependent out-of-phase ac magnetic susceptibility signals were seen for polycrystalline samples at \(\sim 2\) 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 platelet \(\sim 1 \times 0.1 \text{ mm}\) single crystal of complex 2 at five different temperatures between 0.426 and 2.21 K employing a Faraday magnetometer equipped with a 3He 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 \(-2.0 \text{ T}\), a large step is seen at zero field, with a less pronounced step seen at \(-0.55 \text{ T}\).

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 \(S = \frac{7}{2}\) molecule in zero field is shown in Figure 2. Saturation in a +2.0 T field leads to a stabilization in energy of the \(m_s = \frac{-7}{2}\) state and a destabilization of the \(m_s = \frac{7}{2}\) state. As the field is cycled from +2.0 T to \(-2.0 \text{ T}\) 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 \(\Delta H = -D\Delta g\mu_B\), where \(g\) is the EPR g-factor and \(\mu_B\) is the Bohr magneton. The parameter \(D\) gauges the magnitude of axial zero-field splitting (\(\Delta S_{z/2}\)) present in the \(S = \frac{7}{2}\) ground state of complex 2. From the first-derivative plot in Figure 1, the average field interval between steps is calculated to be \(\Delta H = 0.55 \text{ T}\). This gives a value of \(D\Delta g = -0.25 \text{ cm}^{-1}\), which is consistent with the \(D\Delta g = -0.18 \text{ cm}^{-1}\) obtained for this compound by fitting variable-field magnetization data26 and also with fitting of high-field EPR data (\(D\Delta g = -0.25 \text{ cm}^{-1}\)).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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lowest temperature (independent of temperature with a tunneling rate equal to 348 min and was measured in the range of 2.0 to magnetization easy axis of the crystal. One complete hysteresis loop took to give a solid wax cube. The external field was applied parallel to the magnetization curves occur are visible in the first-derivative plots. at 0.53 K is shown. The magnetic fields at which steps in the figure, the first derivative of the smoothed magnetization curves measured a magnetic field.28,29 The two minima: one at zero field and the other at

However, the plot of peak temperature vs. H (Figure 3) shows as the dc field is increased a monotonic decrease in peak temperature would result since the barrier height is decreasing.

derived energy. A peak occurs when the relaxation rate of the molecule matches the frequency of the ac measuring field. If only a single 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) Mn12 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 ms = ±9/2 states comprise a Kramers degenerate pair in zero field. Thus, a S = 9/2 molecule should not be able to tunnel coherently between the mS = −9/2 and mS = +9/2 levels. There is a small internal magnetic field established by the nuclear spins of the Mn ions (I = 7/2) 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 Mn4 molecules in zero external field.

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