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Magnetization tunneling in Mn\(_{12}\) and Mn\(_4\) single-molecule magnets

J. Yoo, E. M. Rumberger, and D. N. Hendrickson
Department of Chemistry and Biochemistry-0358, University of California at San Diego, La Jolla, California 92039-0358

A. Yamaguchi and H. Ishimoto
Institute for Solid State Physics, The University of Tokyo, 7-22-1 Roppongi, Minatoku, Tokyo 106-8666, Japan

E. K. Brechin and G. Christou
Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200

The quantum mechanical tunneling of the direction of magnetization is discussed for several examples of single-molecule magnets (SMMs). SMMs are molecules that function as nanomagnets. Magnetization tunneling is described for two crystallographically different forms of \([\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]\)·solvate. The two Mn\(_{12}\) complexes are isomers, differing both in the positioning of the H\(_2\)O and carboxylate ligands and also in the orientations of the Jahn-Teller elongation at the Mn\(^{III}\) ions. The magnetization vs magnetic field hysteresis loops are quite different for the two isomeric Mn\(_{12}\) complexes. Frequency-dependent ac magnetic susceptibility and dc magnetization decay data are presented to characterize the magnetization relaxation rate vs temperature responses of two mixed-valence Mn\(_4\) complexes. In both cases the Arrhenius plot of the logarithm of the magnetization relaxation rate vs the inverse absolute temperature shows a temperature-dependent region as well as a temperature-independent region.


I. INTRODUCTION

It was discovered in 1993 that

\[\text{[Mn}_{12}\text{O}_{12}(\text{O}_2\text{Me})_{16}(\text{H}_2\text{O})_4]\cdot4\text{H}_2\text{O}\cdot2\text{MeCOOH}\] (1)

functions as a nanoscale magnet.\(^1,2\) Such a molecule has been called\(^3\) a single-molecule magnet (SMM). There has been considerable interest in the magnetic properties of complex 1,\(^4\) which has an \(S=10\) ground state split by axial zero-field splitting (\(D\text{S}_2\)), where \(D=-0.5\text{ cm}^{-1}\). In 1996, it was reported\(^5,6\) that complex 1 exhibits quantum mechanical tunneling of the direction of magnetization. The number of known single-molecule magnets is limited. Polynuclear metal complexes with the composition Mn\(^{IV}\)Mn\(^{III}\), Mn\(^{IV}\)Mn\(^{II}\)Mn\(^{III}\), Mn\(^{IV}\)Mn\(^{II}\), Mn\(^{III}\)Mn\(^{II}\), Mn\(^{II}\)Mn\(^{II}\), Mn\(^{III}\), Mn\(^{II}\), Fe\(^{III}\), and Fe\(^{II}\), have been identified as SMM’s.

Each SMM functions as a superparamagnet as a result of having a large-spin ground state with appreciable magnetoanisotropy. At temperatures below the “blocking temperature” the magnetic moment of a SMM changes sluggishly from “spin up” to “spin down.” It is important to emphasize that the SMM phenomenon arises from the behavior of individual isolated molecules.

A SMM has a potential-energy barrier for reversal of its magnetic moment. It has been found that, in addition to thermal activation of each SMM over the barrier, the reversal of the direction of magnetization also occurs via quantum mechanical tunneling through the barrier.\(^7\) In this paper we will discuss some recent observations on SMM’s that are manifestations of magnetization tunneling.

II. EXPERIMENTAL RESULTS

The occurrence of magnetization tunneling is discussed for two Mn\(^{IV}\)Mn\(^{III}\) and two Mn\(^{II}\)Mn\(^{II}\) complexes. The complexes have the following formulas:

\[\text{[Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_6\text{H}_4-p\text{-Me})_{16}(\text{H}_2\text{O})_4]\cdot(\text{HO}_2\text{CC}_6\text{H}_4-p\text{-Me}).\] (2)

\[\text{[Mn}_{12}\text{O}_{12}(\text{O}_2\text{CC}_6\text{H}_4-p\text{-Me})_{16}(\text{H}_2\text{O})_4]\cdot3\text{H}_2\text{O}.\] (3)

\[\text{[Mn}_4\text{(OAc)}_2(\text{pdmh})_6(\text{H}_2\text{O})_4][\text{ClO}_4]_2,\] (4)

\[\text{[Mn}_4(\text{hmp})_6(\text{Et}_2\text{O})_2][\text{Br}_2].4\text{H}_2\text{O}.\] (5)

In the case of complex 4 ·2MeCN·Et\(_2\)O, the cation sits on a planar Mn\(_4\) rhombus that is mixed-valent Mn\(^{III}\)Mn\(^{II}\). This solvated complex readily loses acetoni-trile to give complex 4 that has an \(S=8\) ground state. Complex 5 consists of a planar Mn\(_4\) rhombus and has a \(S=9\) ground state.

Complexes 2 and 3 have the well known \([\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]\) structure as has been reported\(^2,3\) previously for the benzoate (\(R=\text{-C}_6\text{H}_5\)) and propionate (\(R=\text{-CH}_2\text{CH}_3\)) complexes. As a result of the different solvate molecules in the two crystals, complex 2 crystallizes in the \(C2/c\) space group, whereas complex 3 crystallizes in the \(I2/a\) space group. Even though both of these complexes have the same ligands on the Mn\(_{12}\) complexes, there are two significant differences in the molecular structures of the Mn\(_{12}\) molecules in 2 and 3. First, complexes 2 and 3 differ in the positioning of the four H\(_2\)O ligands. The two Mn\(_{12}\) complexes are geometrical isomers with two different positionings of the H\(_2\)O and \(~\text{O}_2\text{CC}_6\text{H}_4-p\text{-Me}\) ligands. Complexes 2 and 3 have one other very important difference in their struct-
Each Mn$^{llll}$ ion experiences a Jahn-Teller (JT) elongation. All of the JT elongation axes in the hydrate complex 3 are roughly parallel and perpendicular to the plane of the disklike Mn$_{12}$O$_{12}$ core. For complex 2, however, one JT axis is abnormally oriented towards a core O$^{2-}$ ion.

Complexes 2 and 3 have $S=10$ ground states, where the combination of a large spin and anisotropy leads to a potential-energy barrier for reversal of the direction of magnetization. Zero-field interactions split the $S=10$ state into the $M_s=\pm 10, \pm 9, \pm 8, \ldots, \pm 1$ levels. The $M_s=\pm 10$ state can be viewed as the “spin up” state and the $M_s=\pm 10$ state as the “spin down” state. The double-well diagram of Fig. 1 shows how the potential energy of one molecule changes as it reverses its direction of magnetization from “spin up” to “spin down.” The potential-energy barrier is given as $U = |DS_z^2|$, where $DS_z^2$ gauges the axial zero-field splitting in the $S=10$ ground state.

Since complexes 2 and 3 have barriers for changing their magnetic moments from “spin up” to “spin down,” it is informative to examine the change in the magnetization of a sample as an external field is changed. For an oriented sample, steps can be seen at regular intervals of magnetic field in the magnetization hysteresis loop of a SMM. These steps result from a quantum mechanical tunneling of the magnetization. Oriented samples of complexes 2 and 3 were prepared by suspending a few small crystals of either complex in an eicosane wax cube.

Figure 1 shows the magnetization hysteresis data measured for complex 3 at 1.90 K. Magnetization hysteresis loops were determined in the 1.72–2.50 K range. The coercive magnetic field and consequently the area enclosed within a hysteresis loop increase as the temperature is decreased. At 1.72 K the coercive magnetic field for complex 7 is $\approx 2$ T.

Magnetization hysteresis loops were also measured for the oriented eicosane cube of complex 2 at the temperatures of 1.72, 2.20, 2.00, 1.90, and 1.80 K (the 1.90 K data are shown in Fig. 1). The hysteresis loops for complex 2 look quite different than those for complex 3. When the external field is reduced from $\pm 2.5$ T to zero, the magnetization falls off dramatically. The coercive fields are considerably less for complex 2 than for complex 3. These two $p$-methylbenzoate Mn$_{12}$ complexes experience quite different kinetic barriers for reversal of magnetization. It must be emphasized that the sweep rate for all the loops was 25 Oe/s.

From the hysteresis loop data it is clear that the $p$-methylbenzoate complex 2 has an appreciably greater rate of magnetization relaxation than does isomeric complex 3. This can be quantified by analyzing the frequency dependencies of the out-of-phase ac susceptibilities. Ac susceptibility data were collected at 8 different frequencies from 1.0 Hz to 1512 Hz for complex 3. From the peaks in the $\chi''$ vs temperature plots values of the magnetization relaxation time $\tau$ were determined at 8 temperatures. These data give a straight line Arrhenius plot of $\ln(1/\tau)$ vs the inverse absolute temperature ($1/T$) for complex 3. The data were least-squares fit to the Arrhenius equation to give the parameters of $\tau_0 = 7.7 \times 10^{-9}$ s and $U_{eff} = 64$ K. A similar analysis of the frequency dependence of the ac data for complex 2 gives $\tau_0 = 2.0 \times 10^{-10}$ s and $U_{eff} = 38$ K. The activation energy ($U_{eff}$) for reversal of the direction of the magnetization for complex 2 ($U_{eff} = 38$ K) is considerably less than that ($U_{eff} = 64$ K) for the isomeric complex 3. The Mn$_{12}$O$_{12}$ acetate complex 1 has been reported$^5$ to have a $U_{eff}$ value of 62 K, very close to the value for complex 3.

It is likely that the appreciably faster rate of magnetization tunneling observed for complex 2 compared to the isomeric complex 3 is due to the lower symmetry observed for complex 2. This lowered symmetry would increase the rhombic zero-field splitting $[E(S^2_z - S^2_x)]$ in the $S=10$ ground state of complex 2 leading to an increase in the rate of magnetization tunneling.

Variable-field magnetization data have been fit to determine that complex 4 has an $S=8$ ground state$^7$ with $D/k_B = -0.358$ K. Ac magnetic susceptibility measurements were carried out by cooling the sample with a $^3$He-$^4$He dilution refrigerator in the 0.04–3.5 K range. Eleven different ac frequencies were used in the 1.1–995 Hz range, which gave rates of magnetization reversal at 11 different temperatures. These relaxation data fit well to the Arrhenius equation to give an activation energy for magnetization reversal of $U_{eff} = 17.3$ K with a pre-exponential factor of $\tau_0 = 2.54 \times 10^{-7}$ s. The thermodynamic barrier can be calculated to be $U = 22.4$ K. As with other SMMs, it is expected that $U > U_{eff}$, for the reversal of magnetization not only involves a thermal activation over the potential-energy barrier, but also quantum tunneling of the direction of magnetization.

The most definitive data showing that complex 4 does reverse its magnetization direction by quantum tunneling were obtained by means of magnetization decay experiments. In a dc magnetization decay experiment the sample is
Magnetization relaxation below this temperature is occurring purely by a quantum tunneling phenomenon. Complex 4 tunnels between the \( M_s = -8 \) and \( M_s = +8 \) levels at a rate of approximately \( 1 \times 10^{-4} \) s\(^{-1}\).

Magnetization relaxation decay data were also collected for a sample of complex 5 in the 0.047–1.195 K range. This complex has an \( S = 9 \) ground state. The decay data were least-squares fit to give relaxation rates in the above temperature range. These rates were combined with those obtained at higher temperatures by means of the ac susceptibility. At the higher temperatures the relaxation rate is temperature dependent with an activation energy of 15.8 K. At the lower temperatures we again see a temperature-independent rate of relaxation. This is surely attributable to ground state magnetization tunneling. The temperature-independent magnetization tunneling rate is \( 1 \times 10^{-1} \) s\(^{-1}\) for complex 5. Preliminary HFePR data indicate that complex 5 experiences a larger rhombic field splitting than does complex 4. This would explain the faster rate of tunneling in complex 5. Further experimentation is needed on these interesting tetranuclear manganese SMMs to understand in detail the mechanism of magnetization tunneling in these complexes.

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