Resonant magnetization tunnelling in the half-integer-spin single-molecule magnet $[PPh_4][Mn_{12}O_{12}(O_2CEt)_{16}(H_2O)_4]$

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Steps are observed on the magnetization hysteresis loop for an oriented crystal sample of $[PPh_4][Mn_{12}O_{12}(O_2CEt)_{16}(H_2O)_4]$ and these are taken as evidence for field-tuned resonant magnetization tunnelling between quantum levels of the $S = 19/2$ ground state.

The interest in single-molecule magnets (SMM) is growing.[1,2] A SMM has a large spin ground state with such a large magnetic anisotropy that an individual molecule exhibits hysteresis in its magnetization *vs.* external field response. The first SMM reported[3–5] is neutral $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]\cdot 2(HO_2CMe)\cdot 4H_2O$ **1** (denoted Mn_{12}-acetate), which has an $S = 10$ ground state. Molecules possessing Mn_{12},[6] Mn_4,[7] Fe_8,[8] and V_4[9] metal contents have been found to function as SMM. Recently, Friedman *et al.*[10] reported the initial observation of resonant magnetization tunnelling for Mn_{12}-acetate; steps were observed at regular intervals of magnetic field in the magnetization hysteresis loop for oriented crystals. Here, we report the observation of steps in the hysteresis loop for oriented crystals of the salt $[PPh_4][Mn_{12}O_{12}(O_2CEt)_{16}(H_2O)_4]$ **2**. In previous work we have shown[11] the $[Mn_{12}]^-$ anions in **2** have an $S = 19/2$ ground state. The observation of resonant quantum tunnelling in this salt is of considerable interest since a half-integer-spin system should not tunnel coherently in the absence of a magnetic field.[12,13]

In solution, it is possible to add a single electron to a Mn_{12} molecule, and the X-ray crystal structure[11] for complex **2** shows that the added electron is localized on an outer (originally Mn^{3+}) ion rather than an inner (cubane) Mn^{4+} ion, producing a trapped-valence Mn^{2+}, $Mn^{3+}{}_7$, $Mn^{4+}{}_4$ anion in the crystal. The $[Mn_{12}]^-$ anion has an $S = 19/2$ ground state with the double-well potential energy diagram shown in Fig. 1. There are 20 different states with $m_s = \pm 19/2, \pm 17/2 \ldots, \pm 1/2$. The double well represents the change in potential energy of one $[Mn_{12}]^-$ anion in zero field as the anion changes the direction of its magnetic moment from 'spin up' (parallel to z-axis) where $m_s = +19/2$ to 'spin down' (antiparallel to z-axis) where $m_s = -19/2$. The barrier height U is $90|D|$, where D is the parameter characterizing the axial zero-field splitting (DS_z^2) in the $S = 19/2$ ground state.

The rate of relaxation of the magnetization was measured for a polycrystalline sample of **2** equilibrated at one of five temperatures in the range 1.8–2.5 K in an external magnetic field of 3.5 T; the latter was then quenched to zero. The decrease in the magnetization measured at each temperature was fitted to a distribution of single exponentials to give the relaxation rate. Relaxation rates were also determined in the range 3.2–7.2 K by means of ac magnetic susceptibility measurements in zero dc field. At a fixed temperature, the in-phase (χ_M') and out-of-phase (χ_M'') components of magnetic susceptibility were measured as the frequency of the ac field (0.05 Oe) was varied from 0.01 to 1500 Hz. The relaxation time (τ) at a given temperature was determined by fitting the data to eqn. (1),[14] where ω is the angular frequency ($2\pi\nu$), χ_S is the adiabatic susceptibility (*i.e.* $\omega \rightarrow \infty$) and χ_T is the isothermal

$$\chi_M' = \chi_S + (\chi_T - \chi_S)/(1 + \omega^2\tau^2) \qquad (1)$$

susceptibility (*i.e.* $\omega \rightarrow 0$). The relaxation rates vary from $3.94 \times 10^4\ s^{-1}$ at 7.2 K to $6.19 \times 10^{-6}\ s^{-1}$ at 1.8 K. Fig. 2 shows an Arrhenius plot of $\ln(1/\tau)$ *vs.* $1/T$. These data were fit to the Arrhenius law to give a barrier height, U, of 60.2 K with a pre-exponential ($1/\tau_0$) of $1.31 \times 10^8\ s^{-1}$. This compares with $U = 61–67$ K and $1/\tau_0 \simeq 10^7\ s^{-1}$ found[4,5] for the $S = 10$ molecule, Mn_{12}-acetate.

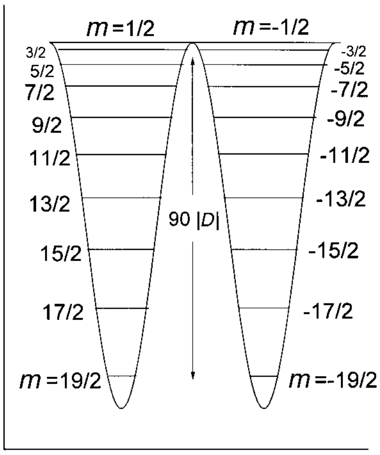

Fig. 1 Plot of potential energy *vs.* the magnetization direction for a single molecule with an $S = 19/2$ ground state in zero magnetic field. Axial zero-field interactions split the $S = 19/2$ state into $m = \pm 19/2, \pm 17/2, \ldots, \pm 1/2$ levels.

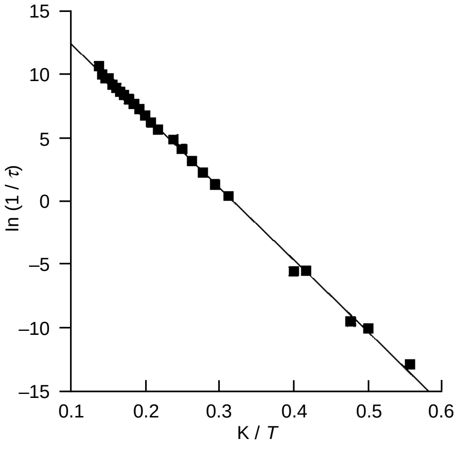

Fig. 2 Plot of the logarithm of the rate of relaxation *vs.* the inverse absolute temperature for $[PPh_4][Mn_{12}O_{12}(O_2CEt)_{16}(H_2O)_4]$ **2**

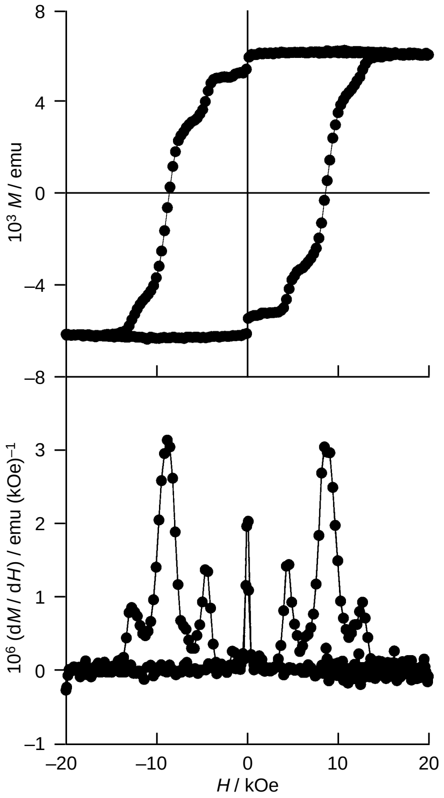

Fig. 3 The top plot shows the magnetization hysteresis loop measured at 1.85 K for five crystals of $[PPh_4][Mn_{12}O_{12}(O_2CEt)_{16}(H_2O)_4]$ **2** oriented in an eicosane wax matrix. In the lower plot is shown a plot of the first derivative of the magnetization hysteresis loop.

Five small crystals ($3 \times 0.1 \times 0.1$ mm) of **2**, grown from CH_2Cl_2–hexanes, were suspended in eicosane held at 40 °C and the suspension introduced into a 5.5 T field, whereupon the five crystals were oriented each with its easy axis parallel to the field. The eicosane was then cooled to room temperature, to give a solid wax cube with the five crystals oriented with parallel easy axes. Fig. 3 shows the hysteresis loop taken at 1.85 K with the magnetic field applied along the easy axes of the crystals. The sample was first saturated in a field of +2.0 T, and the field then swept down to -2.0 T, and cycled back to +2.0 T. The rate of change of the field was 25 Oe s^{-1} and each data point was measured within a few milliseconds. The whole hysteresis loop was collected in 1 h. Steps can clearly be seen on the hysteresis loop, as was reported[10] for the neutral molecule, Mn_{12}-acetate. In the lower part of Fig. 3 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 -0.4686, -0.9022 and -1.262 T. The steps correspond to increases in the rate of change of the magnetization, and are attributable to resonant tunnelling between quantum spin states. With reference to Fig. 1, a +2.0 T field leads to a stabilization in energy of the $m_s = -19/2$ and a destabilization of the $m_s = +19/2$ state. When there is saturation, all of the molecules are in the $m_s = -19/2$ state. As the field is decreased, the first step in the hysteresis loop is seen at zero field. Resonant tunneling occurs because the m_s levels on the right-hand side of the double well have the same energies as the m_s levels on the left.

The simplest Hamiltonian for $[PPh_4][Mn_{12}O_{12}(O_2CEt)_{16}(H_2O)_4]$ **2** is given by eqn. (2).

$$\hat{H} = -D\hat{S}_z^2 - g\mu_B\hat{S}\cdot\hat{H} \qquad (2)$$

If the field is applied along the easy axis, then the eigenstates are $|S, m_s>$. The first term in the Hamiltonian gauges the axial zero-field splitting of the $S = 19/2$ ground state. Physically, this zero-field splitting of the ground state is largely due to the single-ion zero-field splitting at the Mn^{3+} ions in the $[Mn_{12}]^-$ anion. With the above Hamiltonian, it can be shown that the spacings between the steps in the hysteresis loop are given as $\Delta H = -Dn/g\mu_B$, where $n = 0, 1, 2, 3, \ldots$. From Fig. 3, we calculate the average step size to be $\Delta H = 0.42$ T, which gives a value of D/g of 0.20 cm^{-1}, identical to the value obtained for **2** by fitting variable-field magnetization data,[11] and high-field EPR data more recently.

Friedman *et al.*[10] observed six steps for the neutral Mn_{12}-acetate, including the step at zero field, as the field was swept from zero to -3 T after saturation in a +3 T field. We have observed only four steps for the salt **2**, presumably due to the faster relaxation rate of the latter complex. At lower temperatures, more steps should be seen since the relaxation rate will decrease. For both molecular systems, each successive step is seen. This is interesting because the Mn_{12}-acetate molecule has an integer spin ground state with $S = 10$, whereas the $[Mn_{12}]^-$ anion has a half-integer-spin ground state with $S = 19/2$. There have been several papers[12,13] addressing the fact that a molecule with an odd number of unpaired electrons (such as $S = 19/2$) should not exhibit resonant tunnelling in the absence of a magnetic field. For such a molecule, each pair of $\pm m_s$ levels in zero-field exhibits Kramers degeneracy. An $S = 19/2$ molecule should not be able to tunnel coherently between the $m_s = -19/2$ and $m_s = +19/2$ levels, or for that matter, between any m_s and $-m_s$ pair in the absence of a magnetic field. However, clearly the salt of $[Mn_{12}]^-$ shows steps on the hysteresis loop. A possible mechanism for resonant tunneling in this $S = 19/2$ molecule centers around the nuclear spins in the molecule. The ^{55}Mn and ^1H nuclei have spins of $I = 5/2$ and $I = 1/2$, respectively, and this will give rise to a small internal magnetic field (10–200 G) in the molecule. A transverse component of this internal magnetic field may lead to resonant tunnelling for an oriented collection of $[Mn_{12}]^-$ molecules in zero external field.

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Notes and References

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