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# Magnetization tunneling in an enneanuclear manganese cage

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## Abstract

The enneanuclear mixed-valent manganese cage  $[\text{Mn}_9\text{O}_7(\text{OAc})_{11}(\text{thme})(\text{py})_3(\text{H}_2\text{O})_2] \mathbf{1} \{\text{Mn}_9\}$  possesses an  $S = 17/2$  ground state as a result of an antiferromagnetic interaction between three ferromagnetically coupled  $\text{Mn}^{\text{IV}}$  ions and a wheel of four  $\text{Mn}^{\text{III}}$  and two  $\text{Mn}^{\text{II}}$  ions. AC magnetization measurements show a frequency-dependent out-of-phase signal at 3.4 K and 997 Hz, indicative of single-molecule magnetism behaviour. Data obtained from varying the frequency of oscillation of the AC field gives an effective energy barrier ( $U_{\text{eff}}$ ) for the reversal of magnetization of 27 K. Magnetic measurements of single crystals of  $\mathbf{1}$  at low temperature show time- and temperature-dependent hysteresis loops which contain steps at regular intervals of field. DC and AC relaxation measurements show both the temperature-dependent and temperature-independent regions, the latter being definitive evidence of magnetization tunneling in the lowest energy zero-field split component of the ground state.

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**Keywords:** Manganese cages; Single-molecule magnet; Magnetization tunnelling; 1,1,1-Tris(hydroxymethyl)ethane

## 1. Introduction

Individual molecules that possess a combination of a relatively large-spin ground state ( $S$ ) and large and negative magnetoanisotropy (as gauged by the axial zero-field splitting parameter  $D$ ) can, if the temperature is low enough, function as single-molecule magnets (SMMs) [1]. The energy barrier between the spin-up state and the spin-down state is given by  $S^2|D|$  or  $(S^2 - 1/4)^2|D|$  for integer and non-integer spins, respectively, and below the blocking temperature, the relaxation between the two states can be relatively slow and may be observed experimentally as magnetization hysteresis loops, frequency-dependent out-of-phase AC magnetic susceptibility signals or as slow magnetization decay. In addition to this thermally activated relaxation, the

reversal of the direction of magnetization can also occur via quantum mechanical tunneling through the barrier [2]. To date, the best examples of SMMs are all derived from Mn [3–6] and Fe [7] although SMMs containing Ni [8] and V [9] have also been reported. In this paper, we discuss the magnetic properties of the SMM  $[\text{Mn}_9\text{O}_7(\text{OAc})_{11}(\text{thme})(\text{py})_3(\text{H}_2\text{O})_2] \mathbf{1} \{\text{Mn}_9\}$ .

## 2. Experimental

### 2.1. Synthesis

$[\text{Mn}_3\text{O}(\text{OAc})_6(\text{py})_3] \cdot \text{py}$  was dissolved in MeCN with 1 equiv. of the ligand 1,1,1-tris(hydroxymethyl)ethane ( $\text{H}_3\text{thme}$ ) and stirred for 12 h. The solution was then filtered and  $\text{Et}_2\text{O}$  added slowly. Crystals of  $[\text{Mn}_9\text{O}_7(\text{OAc})_{11}(\text{thme})(\text{py})_3(\text{H}_2\text{O})_2] \mathbf{1} \{\text{Mn}_9\}$  were obtained after 1 week. Complex  $\mathbf{1}$  has also been characterized via IR and elemental analysis.

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## 2.2. Physical measurements

DC and AC magnetic susceptibility data were collected on powdered microcrystalline samples on a Quantum Design SQUID magnetometer equipped with a 7T magnet. Diamagnetic corrections were applied using Pascal's constants. Single-crystal magnetic measurements were measured on an array of home-built micro-SQUIDS [10].

## 3. Results and discussion

### 3.1. Description of structure

Complex **1** (Fig. 1) crystallizes in the monoclinic space group  $P2_1/n$  and consists of a  $[\text{Mn}_4^{\text{III}} \text{Mn}_2^{\text{II}} \text{O}_6]^{4+}$  ring on which is sitting a smaller  $[\text{Mn}_3^{\text{IV}} \text{O}]^{10+}$  ring. The

$[\text{Mn}_4^{\text{III}} \text{Mn}_2^{\text{II}} \text{O}_6]^{4+}$  ring is trapped-valence with the  $\text{Mn}^{\text{II}}$  ions being  $\text{Mn}_4$  and  $\text{Mn}_8$ , and the upper  $[\text{Mn}_3\text{O}]^{10+}$  ring consists of only  $\text{Mn}^{4+}$  ions. The upper ring is capped on one side by the sole  $[\text{thme}]^{3-}$  ligand, each arm of which acts as a  $\mu_2$ -bridge, and on the other side by a  $\mu_3$ -oxide (O1). The  $[\text{Mn}_3^{\text{IV}} \text{O}]^{10+}$  unit is connected to the  $[\text{Mn}_4^{\text{III}} \text{Mn}_2^{\text{II}} \text{O}_6]^{4+}$  ring via the six  $\mu_3$ -oxides within the six-membered wheel and three acetates which bridge in their familiar  $\mu_2$ -mode. The remaining acetates in the structure bridge between the Mn ions in the  $[\text{Mn}_4^{\text{III}} \text{Mn}_2^{\text{II}} \text{O}_6]^{4+}$  ring in the same manner. The remaining coordination sites are occupied by two water molecules and three pyridines. All the Mn ions are in distorted octahedral geometries. Jahn–Teller elongations of the  $\text{Mn}^{\text{III}}$  ions ( $\text{Mn}_5$ ,  $\text{Mn}_6$ ,  $\text{Mn}_7$  and  $\text{Mn}_9$ ) all lie perpendicular to the plane of the  $[\text{Mn}_4^{\text{III}} \text{Mn}_2^{\text{II}} \text{O}_6]^{4+}$  ring.

### 3.2. DC magnetic susceptibility

Variable temperature magnetic susceptibility data (Fig. 2) were collected on **1** in the temperature range 300–1.8 K in an applied field of 5 kG. The room temperature  $\chi_M T$  value of  $20 \text{ cm}^3 \text{ K mol}^{-1}$  remains approximately constant until 150 K where it begins to increase to a maximum value of  $36 \text{ cm}^3 \text{ K mol}^{-1}$  at 20 K, before dropping to  $18 \text{ cm}^3 \text{ K mol}^{-1}$  at 1.8 K. The maximum in  $\chi_M T$  is indicative of a high-spin ground state, with the low-temperature decrease assigned to ZFS and/or intermolecular interactions. In order to determine the ground state of **1**, DC magnetization data were collected at 1.8–4 K and 10–70 kG. The data (Fig. 3) were fit to give  $S = 17/2$ ,  $g = 1.97(3)$  and  $D = -0.29 \text{ cm}^{-1}$ . An  $S = 17/2$  ground state can be rationalized by assuming an antiferromagnetic interaction between the ferromagnetically coupled  $\text{Mn}^{\text{IV}}$  ions and the wheel of

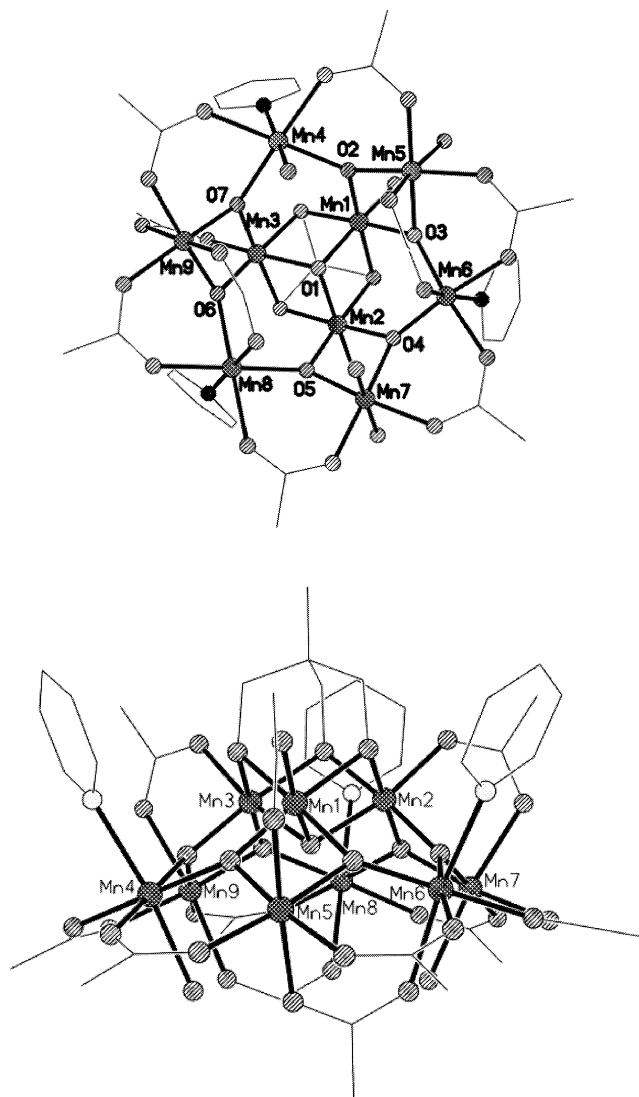


Fig. 1. The structure of **1**.

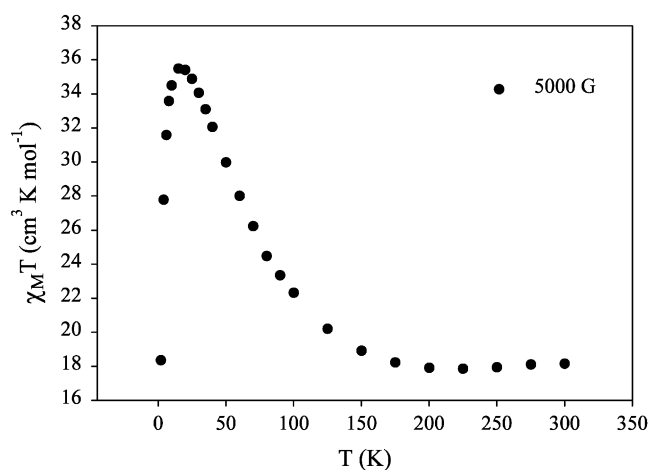


Fig. 2. Variable temperature magnetic susceptibility data for **1**.

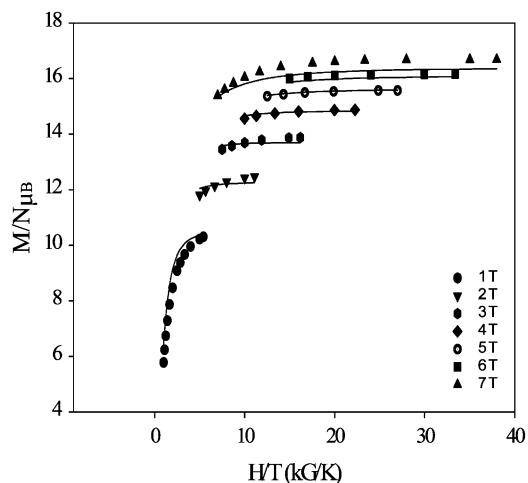


Fig. 3. Plot of reduced magnetization versus  $H/T$  for **1**. The solid lines are fits of the data to an  $S = 17/2$  state with  $g = 1.97$  and  $D = 0.29 \text{ cm}^{-1}$ .

$\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}$  ions, analogous to the situation in the complex  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$ .

### 3.3. AC magnetic susceptibility

AC magnetic susceptibility measurements were taken in the 1.8–10 K range in an AC field oscillating at 50–1000 Hz. The in-phase signal (Fig. 4) shows a frequency-dependent decrease at approximately 4 K, with the out-of-phase signal showing a peak at approximately 3.4 K and 997 Hz (Fig. 4). This behaviour is consistent with that of an SMM. Data obtained by varying the frequency of oscillation of the AC field were fit to the Arrhenius equation giving an effective energy barrier ( $U_{\text{eff}}$ ) of 27 K. The upper limit of the barrier to thermally activated relaxation ( $U$ ) is given by  $(S - 1/4)^2|D|$ , and thus  $U = 30 \text{ K}$  for a system with  $S = 17/2$  and  $D = -0.29 \text{ cm}^{-1}$ . As with other SMMs, the value of  $U$  is expected to be larger than  $U_{\text{eff}}$  since the reversal of magnetization has two components: thermally activated relaxation over the potential energy barrier and quantum tunnelling of magnetization (QTM) through the barrier. Only  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$  [3] derivatives and  $[\text{Mn}_{12}\text{O}_8\text{X}_4(\text{O}_2\text{CPh})_8(\text{hmp})_6]$  [4] have larger or comparable energy barriers for the relaxation of the magnetization.

### 3.4. Single-crystal magnetic measurements

QTM studies were performed on **1** by magnetization measurements on single crystals using an array of micro-SQUIDS.

Relaxation data were determined from DC relaxation decay measurements (Fig. 5). First, a large DC field of 1.4 T was applied to the sample at 5 K to saturate the

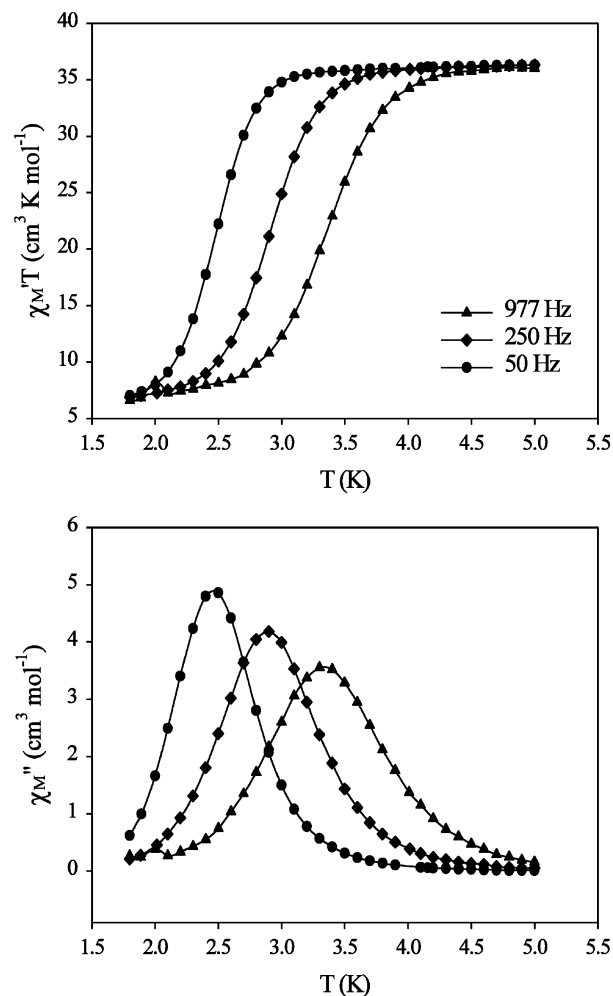


Fig. 4. Plots of the in-phase ( $\chi'_M$ ) signal as  $\chi'_M T$  and out-of-phase ( $\chi''_M$ ) signal in AC susceptibility studies versus  $T$  in a 3.5 G field oscillating at the indicated frequencies.

magnetization in one direction, and the temperature lowered to a specific value between 1.8 and 0.95 K. When the temperature was stable, the field was swept from 1.4 T to zero at a rate of  $0.14 \text{ T s}^{-1}$  and the magnetization in zero field measured as a function of time. Combining this relaxation data with the AC  $\chi_M T$  data allows the construction of an Arrhenius plot of  $\ln \tau$  versus  $1/T$  (Fig. 6). Above approximately 0.4 K, the relaxation rate is temperature-dependent. The straight line in Fig. 6 is a fit to the Arrhenius law yielding  $\tau_0 = 6.5 \times 10^{-8} \text{ s}$  and  $U_{\text{eff}} = 26.6 \text{ K}$ . Below approximately 0.4 K, however, the relaxation rate is temperature-independent with a relaxation rate of  $8 \times 10^6 \text{ s}$ , indicative of QTM between the lowest energy  $M_s = \pm 17/2$  levels of the ground state.

Fig. 7 shows hysteresis loops for **1** at temperatures below 1.5 K and at sweep rates of  $0.001 \text{ T s}^{-1}$ , with the field applied in the direction of the easy-axis of half the molecules. For the other half, the field is approximately

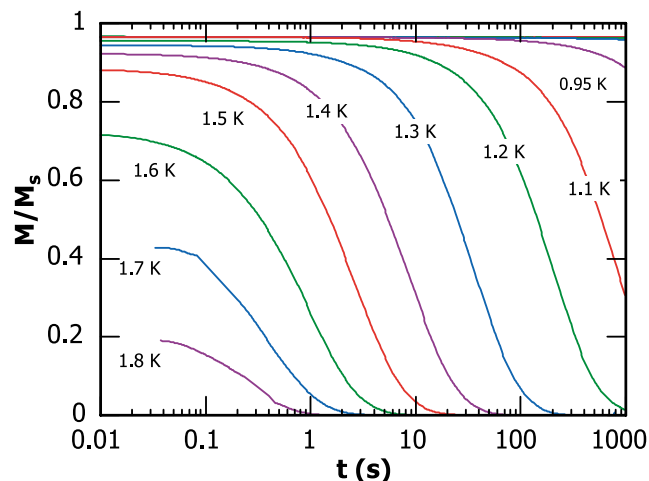


Fig. 5. Relaxation data for **1**, plotted as fraction of maximum value

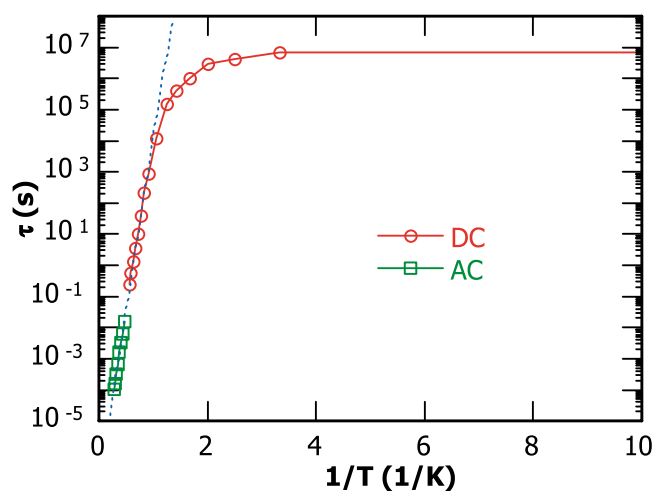
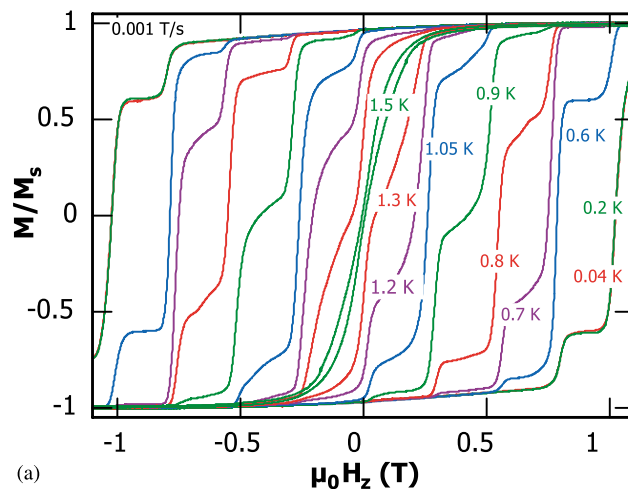


Fig. 6. Arrhenius plot for **1** using AC data ( $\chi''_M$ ) and DC decay data on a single crystal. The solid line is the fit of the data in the thermally activated region and the dashed line the fit of the temperature-independent data.

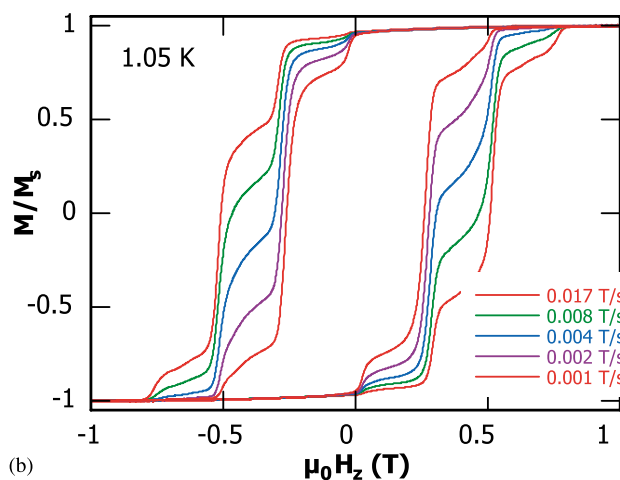
transverse. The hysteresis loops are not smooth, but show steps at regular intervals of field, indicative of resonant QTM. That is, as well as the thermally activated relaxation over the barrier the magnetization is relaxing through the barrier. The field separation between the zero-field resonance and the next is 0.27 T, giving  $D/g = 0.181$  K. If we assume a value of  $g = 2$  then the observed  $D = 0.36$  K is in good agreement with that obtained from the bulk DC measurements.

#### 4. Conclusions

The complex  $\{\text{Mn}_9\}$  **1** has an  $S = 17/2$  ground state as a result of the antiferromagnetic interaction between



(a)



(b)

Fig. 7. Magnetization ( $M$ ) of **1** (plotted as fraction of maximum value  $M_s$ ) versus applied magnetic field ( $\mu_0 H$ ). The resulting hysteresis loops are shown at different temperatures (a) and different field sweep rates (b).

three ferromagnetically coupled  $\text{Mn}^{\text{IV}}$  ions and a wheel of  $\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}$  ions. DC magnetization measurements indicated that  $\{\text{Mn}_9\}$  possesses zero-field splitting with a negative  $D$  value. AC susceptibility studies showed the presence of frequency-dependent out-of-phase peaks with a concomitant decrease in the in-phase signal, diagnostic of an SMM. Single-crystal studies showed hysteresis loops containing steps at regular intervals of field, and temperature-independent relaxation of the magnetization below 0.4 K, indicative of QTM.

#### 5. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 189138. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2

1EZ, UK (fax: +44-1233-336033; email: deposit@ccdc.cam.ac.uk or [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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