

A new class of single-molecule magnet: $[\text{Mn}_9\text{O}_7(\text{OAc})_{11}(\text{thme})(\text{py})_3(\text{H}_2\text{O})_2]$ with an $S = 17/2$ ground state

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The reaction of $[\text{Mn}_3\text{O}(\text{OAc})_6(\text{py})_3]$ with 1,1,1-tris(hydroxymethyl)ethane (H_3thme) gives the $\text{Mn}(\text{IV})_3\text{Mn}(\text{III})_4\text{Mn}(\text{II})_2$ complex $[\text{Mn}_9\text{O}_7(\text{OAc})_{11}(\text{thme})(\text{py})_3(\text{H}_2\text{O})_2]$, which has an $S = 17/2$ ground state and displays strong out-of-phase signals in ac susceptibility studies that establish it as a new class of single-molecule magnet.

The study of molecules with large numbers of unpaired electrons has become the focus of much attention since the discovery that these complexes can function as magnetizable magnets below their blocking temperature.¹ These single-molecule magnets (SMMs) therefore represent an important step forward in the miniaturization of memory storage devices. The SMM behaviour of these complexes results from a combination of a high-spin ground state and easy-axis type magnetoanisotropy, and can be determined experimentally by the observation of frequency-dependent out-of-phase (χ'') signals in ac magnetic susceptibility measurements, and hysteresis loops in magnetization vs. dc field studies. To date, the best SMMs are the family of molecules of formula $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_x]^{n-}$ ($n = 0, 1, 2; x = 3, 4$)²⁻⁴ but there are a number of other examples of SMMs containing manganese,⁵⁻⁷ iron,⁸⁻¹⁰ nickel,¹¹ and vanadium.¹² We herein report a new class of enneanuclear manganese single-molecule magnets with an $S = 17/2$ ground state and a χ'' signal that occurs at higher temperatures than those observed for all previously reported SMMs outside the $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_x]^{n-}$ family.

Reaction of $[\text{Mn}_3\text{O}(\text{OAc})_6(\text{py})_3]$ with 1,1,1-tris(hydroxymethyl)ethane (H_3thme) in MeCN leads to formation of the complex $[\text{Mn}_9\text{O}_7(\text{OAc})_{11}(\text{thme})(\text{py})_3(\text{H}_2\text{O})_2]$, **1**, in yields of $\leq 15\%$. Complex **1**⁺ (Fig. 1) crystallises in the monoclinic space group $P2_1/n$. The core of **1** consists of a $[\text{Mn}^{\text{III}}_4\text{Mn}^{\text{II}}_2\text{O}_6]^{4+}$ ring on which is sitting a smaller $[\text{Mn}^{\text{IV}}_3\text{O}]^{10+}$ ring. The $[\text{Mn}^{\text{III}}_4\text{Mn}^{\text{II}}_2\text{O}_6]^{4+}$ ring is trapped-valence with the Mn^{II} ions being Mn4 and Mn8, and the upper $[\text{Mn}_3\text{O}]^{10+}$ ring consists of only 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 μ_2 -bridge, and on the other side by a μ_3 -oxide (O1). The $[\text{Mn}^{\text{IV}}_3\text{O}]^{10+}$ unit is connected to the $[\text{Mn}^{\text{III}}_4\text{Mn}^{\text{II}}_2\text{O}_6]^{4+}$ ring via the six μ_3 -oxides within the six-membered wheel and three acetates which bridge in their familiar μ_2 -mode. The remaining acetates in the structure bridge between the Mn ions in the $[\text{Mn}^{\text{III}}_4\text{Mn}^{\text{II}}_2\text{O}_6]^{4+}$ 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. All oxidation states were assigned using charge balance considerations, bond lengths and bond valence sum calculations. The Jahn–Teller elongations of the Mn^{III} ions (Mn5, Mn6, Mn7, Mn9) all lie perpendicular to the plane of the $[\text{Mn}^{\text{III}}_4\text{Mn}^{\text{II}}_2\text{O}_6]^{4+}$ ring.

Solid state dc magnetization measurements were performed on **1** in the range 1.8–300 K in a field of 5.0 kG. The $\chi_{\text{M}}T$ value of approximately $20 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K remains approx-

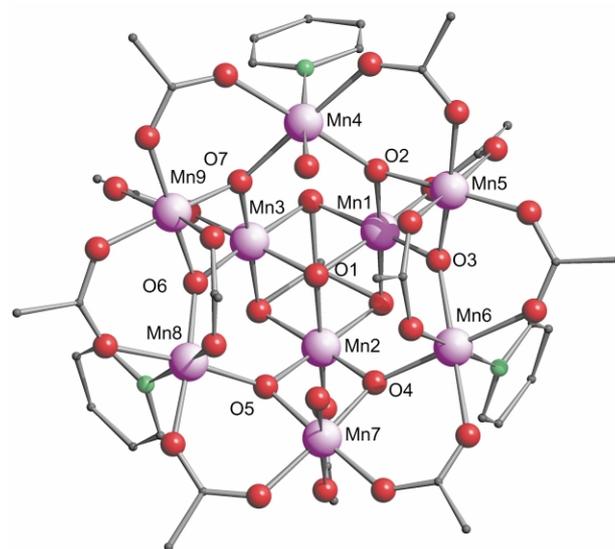


Fig. 1 The structure of complex **1**. Selected inter-atomic distances (Å), $\text{Mn}(\text{IV})\text{--O}$, 1.802(2)–1.992(2); $\text{Mn}(\text{III})\text{--O}$, 1.856(2)–2.237(2); $\text{Mn}(\text{II})\text{--O}$, 2.099(2)–2.282(3).

imately constant as the temperature is decreased until ca. 150 K when it begins to increase to a maximum value of $36 \text{ cm}^3 \text{ K mol}^{-1}$ at 20 K before decreasing rapidly to $18 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K. This suggests that the molecule has a high spin ground state, with the low temperature decrease assigned to zero field splitting and other effects. In order to determine the ground state spin, magnetization data were collected in the ranges 1.8–10 K and 10–70 kG (Fig. 2). The data were fit, assuming only the ground state is populated, giving best fits of $S = 17/2$, $g =$

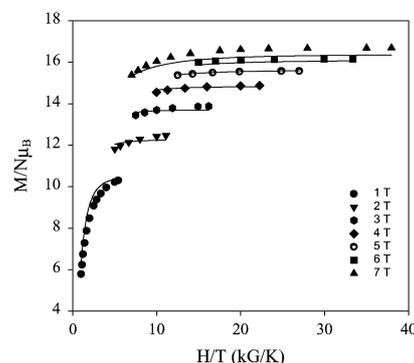


Fig. 2 Plot of reduced magnetization vs. H/T for complex **1**. The solid lines are fits of the data to an $S = 17/2$ state with $g = 2.009$ and $D = -0.29 \text{ cm}^{-1}$.

1.97(3), $D \approx -0.29(3) \text{ cm}^{-1}$ and $S = 19/2$, $g = 1.77(3)$, $D \approx -0.23(3) \text{ cm}^{-1}$, which are of comparable quality. We conclude that **1** has a $S = 17/2$ or $19/2$ ground state, but favour the former since an antiferromagnetic interaction between the three Mn^{4+} ions in the 'inner wheel' and the $\text{Mn}^{3+}/\text{Mn}^{2+}$ ions in the 'outer wheel' would result in a spin value of $S = 17/2$. This would be analogous to the situation in $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$ where the four ferromagnetically-coupled Mn^{4+} ions couple antiferromagnetically with the surrounding eight Mn^{3+} ions resulting in a net spin of $S = 10$.

Ac magnetization measurements were performed on **1** in the 1.8–10 K range in a 3.5 G ac field oscillating at 50–1000 Hz. The in-phase signal (Fig. 3) shows a frequency-dependent decrease at $T \approx 4$ K indicative of the onset of slow magnetic relaxation. The out-of-phase (χ_M'') signal shows a peak at ca. 3.4 K at a 997 Hz ac frequency. The presence of an out-of-phase signal is diagnostic of single-molecule magnetism behaviour and is caused by the inability of **1** to relax quickly enough, at these temperatures, to keep up with the oscillating field. This establishes that **1** is a SMM. Data obtained by varying the frequency of oscillation of the ac field were fit to the Arrhenius equation to obtain the effective energy barrier (U_{eff}) for the relaxation of magnetization. The slope of the Arrhenius plot gives a U_{eff} of 27 K. For a non-integer spin system, the upper limit of the barrier to thermally activated magnetization relaxation (U) is given by $(S^2 - 1/4)|D|$, which for $S = 17/2$ and $D = -0.29 \text{ cm}^{-1}$ (-0.42 K) gives $U = 30 \text{ K}$. The relatively large value of U_{eff} thus makes complex **1** an important new example of a single-molecule magnet. Indeed, only $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$ complexes (and their derivatives, $U_{\text{eff}} \approx 70 \text{ K}$) and $[\text{Mn}_{12}\text{O}_8\text{Cl}_4(\text{O}_2\text{CPh})_8(\text{hmp})_6]$ ($U_{\text{eff}} \approx 30 \text{ K}$) have larger or comparable energy barriers.^{2,7}

In summary, complex **1** represents an interesting new example of a SMM, with a relatively large barrier for the reorientation of magnetization. Work is under way to determine more precisely the value of D (HFEP) along with more detailed low temperature magnetic studies to determine the

degree of hysteresis and quantum tunnelling of magnetization exhibited by **1**. Attempts to oxidise the two Mn^{2+} ions in **1** are also underway, in order to provide a systematic study of the effect of oxidation state on the magnetic properties.

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Notes and references

† Complex **1** analysed satisfactorily (C, H, N) as **1**-MeCN-Et₂O. Crystals were kept in contact with mother liquor to avoid solvent loss and were crystallographically identified as **1**·3MeCN-Et₂O.

‡ *Crystal Data*. Diffraction data were collected with Mo-K α X-radiation ($\lambda = 0.71073 \text{ \AA}$) on a Bruker Smart APEX diffractometer equipped with an Oxford Cryosystems low-temperature device operating at 150 K. An absorption correction was applied using the program SADABS;¹³ the structure was solved using Patterson methods (DIRDIF)¹⁴ and refined by full-matrix least squares against F^2 (SHELXTL)¹⁵ using all unique data. H-Atoms were treated either as part of a rotating rigid group, or with a riding model. A cluster of peaks in the Fourier difference map in the region of the hexagon of oxygen atoms attached to Mn4–9 were interpreted as a three-fold disordered set of two acetates and two coordinated water molecules. The acetates were restrained to be geometrically similar; the major component C-atoms were refined with anisotropic thermal parameters, the minor component only isotropically. Disordered solvent regions were treated in the manner described by van der Sluis and Spek.¹⁵ This treated 276 e per cell, or 69 e per formula unit. This fits quite well with 1MeCN and 1Et₂O (= 66e) for formula unit. The values of $F(000)$, the density, μ , etc. reflect this assumption. Further details are given in the CIF. $\text{C}_{52}\text{H}_{80}\text{Mn}_9\text{N}_6\text{O}_{35}$, $M = 1843.68$, brown blocks, monoclinic, $P2_1/n$, $a = 13.745(3)$, $b = 23.688(5)$, $c = 23.259(5) \text{ \AA}$, $\beta = 96.49(3)^\circ$, $V = 7524(3) \text{ \AA}^3$, $\mu = 1.546 \text{ mm}^{-1}$, 42819 reflections measured, of which 15403 were independent, $\theta_{\text{max}} = 26.42^\circ$, 901 parameters and 163 restraints, $R = 0.0376$ [based on F and 13552 data with $F > 4\sigma(F)$], $R_w = 0.0939$ (based on F^2 and all data), the final difference map extremes were $+0.63$ and -0.34 e \AA^{-3} . CCDC 189138. See <http://www.rsc.org/suppdata/cc/b2/b206386g/> for crystallographic data in CIF or other electronic format.

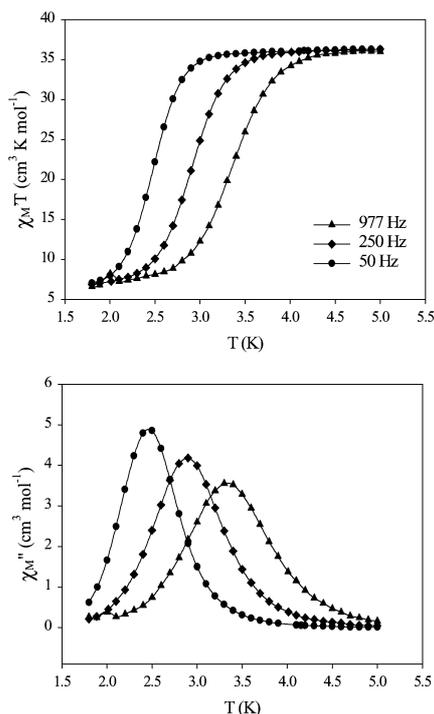


Fig. 3 Plots of the in-phase (χ_M') signal as $\chi_M'T$ and out-of-phase (χ_M'') signal in ac susceptibility studies vs. temperature in a 3.5 G field oscillating at the indicated frequencies.

- R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, 1993, **365**, 141–143.
- R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1993, **115**, 1804–1816.
- H. J. Eppley, H.-L. Tsai, N. de Vries, K. Folting, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1996, **118**, 7746.
- M. Soler, S. K. Chandra, D. Ruiz, E. R. Davidson, D. N. Hendrickson and G. Christou, *Chem. Commun.*, 2000, 2417.
- S. M. J. Aubin, M. W. Wemple, D. M. Adams, H.-L. Tsai, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1996, **118**, 7746.
- E. K. Brechin, J. Yoo, M. Nakano, J. C. Huffman, D. N. Hendrickson and G. Christou, *Chem. Commun.*, 1999, 783.
- C. Boskovic, E. K. Brechin, W. E. Streib, K. Folting, D. N. Hendrickson and G. Christou, *Chem. Commun.*, 2001, 467.
- C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli and D. Gatteschi, *Phys. Rev. Lett.*, 1997, **78**, 4645.
- A.-L. Barra, A. Caneschi, A. Cornia, F. Fabrizi de Biani, D. Gatteschi, C. Sangregorio, R. Sessoli and L. Sorace, *J. Am. Chem. Soc.*, 1999, **121**, 5302.
- C. Benelli, J. Cano, Y. Journaux, R. Sessoli, G. A. Solan and R. E. P. Winpenny, *Inorg. Chem.*, 2001, **40**, 188.
- C. Cadiou, M. Murrie, C. Paulsen, V. Villar, W. Wernsdorfer and R. E. P. Winpenny, *Chem. Commun.*, 2001, 2666.
- S. L. Castro, Z. Sun, C. M. Grant, J. C. Bollinger, D. N. Hendrickson and G. Christou, *J. Am. Chem. Soc.*, 1998, **120**, 2997.
- P. T. Beurskens, G. Beurskens, W. P. Bosman, R. de Gelder, S. Garcia-Granda, R. O. Gould, R. Israel and J. M. M. Smits, Crystallography Laboratory, University of Nijmegen, The Netherlands, 1996.
- G. M. Sheldrick, SHELXTL, version 5, Bruker AXS, Madison, Wisconsin, 1995.
- P. van der Sluis and A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, 194–201. PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, A. L. Spek, 1998. Incorporated into The WinGX suite: L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837–838.