A new class of single-molecule magnets: mixed-valent $[Mn_4(O_2CMe)_2(Hpdm)_6][ClO_4]_2$ with an $S = 8$ ground state

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The reaction of pyridine-2,6-dimethanol (H_2pdm) with $[Mn_3O(O_2CMe)_6(py)_3][ClO_4]$ gives the $2Mn^{II}$, $2Mn^{III}$ title compound 1, which has an $S = 8$ ground state and displays strong out-of-phase signals in ac susceptibility studies that establish 1 as a new class of single-molecule magnet.

The study of molecules with unusually large numbers of unpaired electrons has taken on added impetus in recent years as this area has been identified as the source of a new magnetic phenomenon of relevance to the magnetic materials arena, *i.e.* the ability of molecules below a critical temperature to function as magnetizable magnets.[1–10] Samples of such molecules thus function as collections of extremely small magnetic particles and ones that are of a uniform size distribution in contrast to metal oxide particles (or other magnetic materials) of nanoscale dimensions, which are prepared as a range of particle sizes. To date, $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ ($S = 10$),[1–5] $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]^-$ salts ($S = 19/2$),[6] $[Mn_4O_3X(O_2CMe)_3(dbm)_3]$ ($S = 9/2$; dbm is the anion of dibenzoylmethane),[7,8] $[Fe_8O_2(OH)_{12}(tacn)_6]^{8+}$ (tacn = 1,4,7-triazacyclononane) salts ($S = 10$)[9] and $[V_4O_2(O_2CR)_7(L–L)_2]^z$ ($S = 3$; L–L = 2,2′-bipyridine, pyridine-2-carboxylate anion)[10] are the most well studied examples. A convenient way of detecting the slow magnetic relaxation (reorientation of the magnetic moment or magnetization vector) of a single-molecule magnet (SMM) is by the appearance of an out-of-phase signal (χ_M'') in ac susceptibility studies showing that the relaxation is too slow to keep up with the oscillating field. We herein report access to a new class of Mn-based SMMs with an $S = 8$ ground state and a strong χ_M'' signal, representing an important new addition to this small family of molecules.

The potentially tridentate chelating ligand pyridine-2,6-dimethanol(H_2pdm), or 2,6-bis(hydroxymethyl)pyridine has been little employed[11,12] in metal chemistry but offers interesting possibilities for transition metal cluster chemistry. Reaction of H_2pdm with $[Mn_3O(O_2CMe)_6(py)_3][ClO_4]$ in a 3 : 1 molar ratio in CH_2Cl_2 gives a red–brown solution from which $[Mn_4(O_2CMe)_2(Hpdm)_6][ClO_4]_2$ **1** precipitates within 24 h. The solid can be recrystallized in *ca.* 50% total yield after three days from a MeCN/Et_2O layering. Diffusion of Et_2O directly into an MeCN reaction solution also gives **1** but in only 15% yield after one week. The centrosymmetric cation of **1**†‡ (Fig. 1) consists of a planar, mixed-valence Mn_4 rhombus with Mn(1) and Mn(2) assigned as being Mn^{III} and Mn^{II}, respectively, on the basis of bond valence sum calculations and the presence at Mn(1) of a Jahn–Teller elongation axis [O(17)–Mn(1)–N(30)], as expected for high-spin Mn^{III}. All ligands are thus only mono-deprotonated (*i.e.* Hpdm) as found for this group previously.[11] Two Mn_3 triangular faces are each bridged by a μ_3-oxygen [O(17)] from a bidentate, chelating Hpdm whose protonated [O(23)] is unbound. Two of the remaining groups are also bidentate, with O(27) bridging Mn(1) and Mn(2′) and O(33) not ligated, but the remaining two Hpdm groups are tridentate with protonated O(13) terminally coordinated and O(7) bridging Mn(1) and Mn(2). Two bridging $MeCO_2^-$ groups complete the ligation. The Mn^{II} metal atoms Mn(2) are thus seven-coordinate with distorted pentagonal bipyramidal geometry, whereas Mn(1) is distorted octahedral. There is an intramolecular hydrogen bond between O(13) and O(23) [2.852(9) Å]. The cation of **1** is the first example of the (H)pdm ligand in a bridging mode and suggests that other clusters might be accessible with this versatile ligand.

Solid-state dc magnetization measurements were performed on **1** in the range 5.0–300 K. The effective magnetic moment (μ_{eff}) slowly increases from 10.5 μ_B at 300 K to 12.8 μ_B at 15.0 K, and then decreases to 11.3 μ_B at 5.0 K, suggesting the complex to have a high spin ground state; the low-temperature decrease is assigned to zero-field splitting (ZFS) and Zeeman effects. Owing to the low symmetry of the cation of **1**, it is not possible to use the Kambe approach to fit the μ_{eff} *vs.* T data with the three requisite J values. In order to determine the ground state, therefore, magnetization data were collected in the temperature and magnetic field ranges 2.00–4.00 K and 20.0–50.0 kG (2–5 T) (Fig. 2). Fitting of these data, assuming only the ground state is populated at $T \leqslant 4.00$ K, gave $S = 8$, $g = 1.85(3)$ and $D = -0.25(3)$ cm^{-1}, where D is the axial ZFS parameter. Thus, **1** is a new example of a species with an unusually large spin.

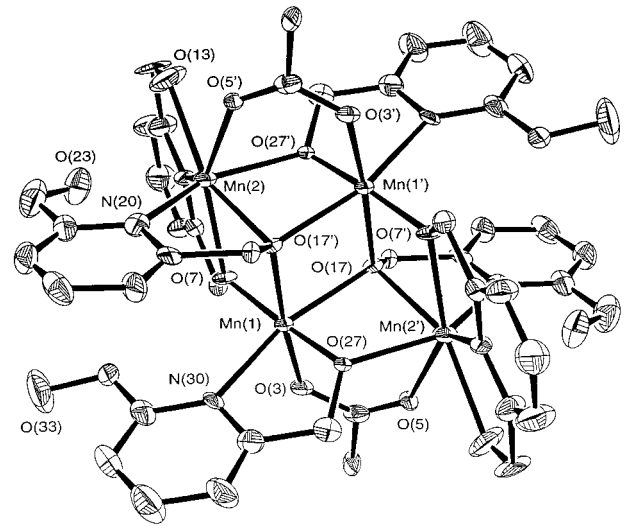

Fig. 1 ORTEP plot with 50% probability ellipsoids of the cation of **1**. Selected interatomic distances (Å) and angles (°): Mn(1)···Mn(1′) 3.253(2), Mn(1)···Mn(2) 3.351(2), Mn(1)···Mn(2′) 3.284(2), Mn(1)–O(7) 1.879(5), Mn(1)–O(17′) 1.967(4), Mn(1)–O(17) 2.264(4), Mn(1)–O(27) 1.873(5), Mn(2)–O(7) 2.271(4), Mn(2)–O(17) 2.300(5), Mn(2)–O(27′) 2.227(4); Mn(1)–O(17)–Mn(1′) 100.27(17), Mn(1)–O(17′)–Mn(2) 103.24(20), Mn(1′)–O(17′)–Mn(2) 92.03(16), Mn(1)–O(7)–Mn(2) 107.30(23), Mn(1′)–O(27′)–Mn(2) 106.13(22).

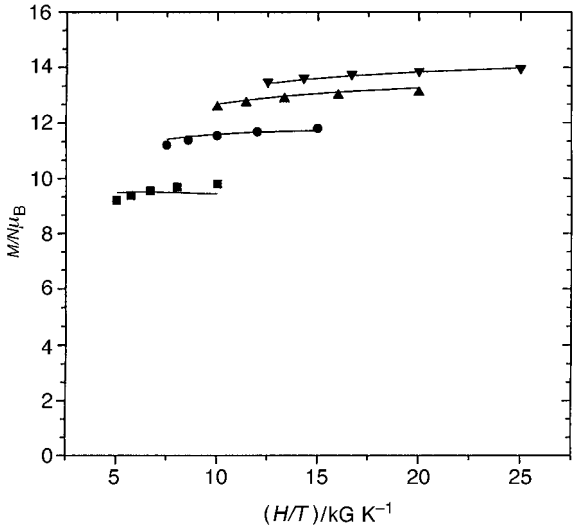

Fig. 2 Plot of reduced magnetization *vs.* *H/T* for complex **1**. The solid lines are fits of the data to an $S = 8$ state with $g = 1.85$ and $D = -0.25$ cm^{-1}. Data were measured at 20 (■), 30 (●), 40 (▲) and 50 kG (▼).

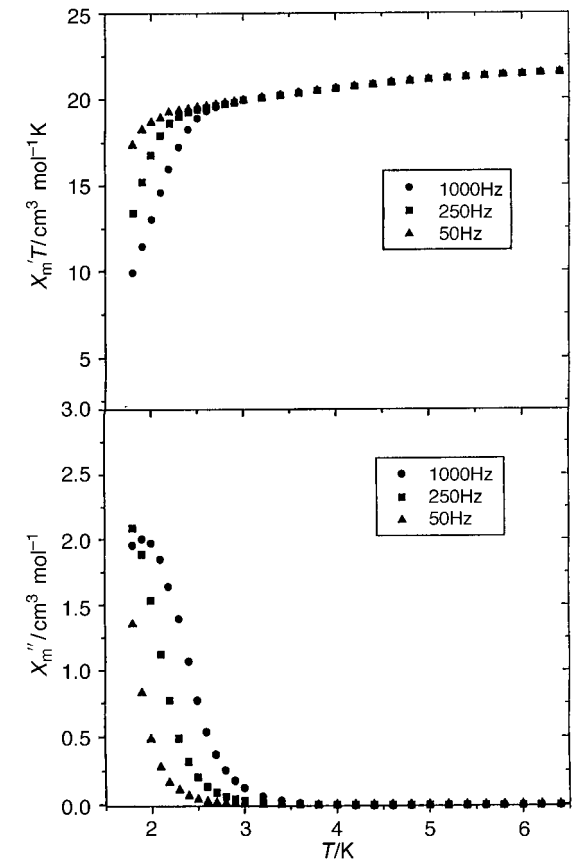

Fig. 3 Plots of the in-phase (χ_M') signal as $\chi_M'T$ and out-of-phase (χ_M'') signal in ac susceptibility studies *vs.* temperature in a 1 G field oscillating at the indicated frequencies.

Complex **1** appeared a good candidate for ac susceptibility studies to determine if it displays the slow magnetization relaxation characteristic of a single-molecule magnet; data were thus collected in the range 1.8–6.4 K range in a 1 G ac field oscillating at 50–1000 Hz. The barrier to thermally activated magnetization relaxation is $S^2|D|$ for an integer spin system, which is 16 cm^{-1} for $S = 8$ and $D = -0.25$ cm^{-1}, a value that is significant compared with thermal energy at low temperature. Indeed, the in-phase $\chi_M'T$ signal (Fig. 3) shows a frequency-dependent decrease at $T < 3.5$ K indicative of the onset of slow relaxation, and this was confirmed by the appearance of an out-of-phase (χ_M'') signal showing that **1** cannot relax fast enough at these temperatures to keep in phase with the oscillating field. The χ_M'' signal is strong, with a peak evident at *ca.* 2 K at a 1000 Hz ac frequency; the peak position corresponds to the temperature at which the relaxation rate is equal to the ac oscillation frequency. A preliminary analysis of the χ_M'' data indicates that the barrier for magnetization relaxation is 12(2) cm^{-1}, in keeping with the presence of magnetization tunnelling. Complex **1** is only the third structural type to show such a strong χ_M'' signal with a peak at $T \geqslant 2$ K, the others being the complexes $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]^{0,-}$ and $[Mn_4O_3X(O_2C\text{-}Me)_3(dbm)_3]$, and this indicates **1** to be a particularly welcome new addition to this small but growing class of molecules. It also emphasizes that oxide (O^{2-}) bridged clusters are not the sole source of the SMM family of complexes. Efforts are in progress to fit the μ_{eff} *vs.* T data for **1** by a matrix diagonalization approach to determine the individual pairwise exchange interactions, as well as extending studies to $T < 1.8$ K to investigate the degree of hysteresis exhibited by **1**.

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Notes and references

† The complex analysed satisfactorily (C, H, N) as solvent-free. Crystals were kept in contact with mother liquor to avoid solvent loss and were crystallographically identified as **1**·2MeCN.*x*Et$_2$O.

‡ *Crystal data*: $C_{50}H_{60}Cl_2Mn_4N_8O_{24}$ (excl. solv.), $M_r = 1447.75$, triclinic, space group $P\bar{1}$ $a = 11.914(3)$, $b = 15.342(4)$, $c = 9.660(3)$ Å, $\alpha = 104.58(1)$, $\beta = 93.42(1)$, $\gamma = 106.06(1)°$, $U = 1626(3)$ Å^3, $Z = 1$, $T = 105$ K. Residuals R and R_w were 0.0871 and 0.0679, respectively, from refinement on F using 3038 unique data with $F > 2.33\sigma(F)$. The solv group(s) comprised a total of seven peaks (of occupancy *ca.* 50%) assigned to a badly disordered Et$_2$O molecule. CCDC 182/1203. See http://www.rsc.org/suppdata/cc/1999/783/ for crystallographic files in .cif format.

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