A new class of single-molecule magnets: mixed-valent
\([\text{Mn}_4(\text{O}_2\text{CMe})_2(\text{Hpdm})_3][\text{ClO}_4]_2\) with an \(S = 8\) ground state

Euan K. Brechin,∗a Jae Yoo,†b Motohiro Nakano,‡b John C. Huffman,∗a David N. Hendrickson‡b and George Christou∗a

Figure 1

The reaction of pyridine-2,6-dimethanol (H₂pdm) with
\([\text{Mn}_3\text{O}(\text{O}_2\text{CMe})_6(\text{py})_3][\text{ClO}_4]_2\) gives the 2MnII, 2MnIII 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, \([\text{Mn}_2\text{O}_2\text{Cr}(\text{H}_2\text{O})_4][\text{ClO}_4]_2\) \((S = 10)\),1–5 \([\text{Mn}_2\text{O}_2\text{Cr}(\text{H}_2\text{O})_4][\text{ClO}_4]_2\) \((S = 9)\);2 dbm is the anion of dibenzoylmethane,7,8
\([\text{Os}_8\text{O}_2(\text{OH})_12(\text{tacn})_6]^{8+\text{[tacn = 1,4,7-triazacyclononane}}\) salts
\((S = 10)\) and \([\text{V}_4\text{O}_2(\text{O}_2\text{CR})_7(\text{L–L})_2][\text{ClO}_4]_2\) \((S = 3 / L-L = 2,2'\text{bipyridine, pyridine-2-carboxylate anion})\) are the most well
studied examples. A convenient way of detecting the slow
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while sweeping the external field. Slow magnetic relaxation is
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The potentially tridentate chelating ligand pyridine-2,6-di-
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the first example of the (H)pdm ligand in a bridging mode and
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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 ($\mu$T), 30 ($\mu$T), 40 ($\mu$T) and 50 kG ($\mu$T).

Fig. 3 Plots of the in-phase ($\chi_M''$) signal and out-of-phase ($\chi_M'$) signal in ac susceptibility studies vs. temperature in a 1 G field oscillating at 1000 Hz for complex 1.

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 $\chi_M''$ 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 ($\chi_M'$) signal showing that 1 cannot relax fast enough at these temperatures to keep in phase with the oscillating field. The $\chi_M''$ 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 $\chi_M''$ 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 strong $\chi_M''$ signal with a peak at $T \approx 2$ K, the others being the complexes $\left[\text{Mn}_2\text{O}_2\text{Cr}((\text{O}_2\text{CR})_2\text{H}_2\text{O})_4\right]^{2-}$ and $\left[\text{Mn}_3\text{O}_3\text{X}((\text{O}_2\text{C})\text{Me}_2)_4(\text{dbm})_4\right]$, 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 $\mu$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.

This work was supported by the National Science Foundation.

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 $\text{C}_2\text{MeCN}.\text{Et}_2\text{O}$. Crystals were grown by slow evaporation of a 1:1:2 MeCN:Et$_2$O.

† Crystal data: $\text{C}_{50}\text{H}_{60}\text{Cl}_2\text{Mn}_4\text{N}_8\text{O}_{24}$ (excl. solv.), $M_r = 1447.75$, triclinic, space group $P\overline{1}$, $a = 11.914(3)$, $b = 15.342(4)$, $c = 9.660(3)$ 'A, $\alpha = 104.58(1)$, $\beta = 93.42(1)$, $\gamma = 106.06(1)$, $U = 16263.6$ 'A$^3$, $Z = 1$, $T = 105$ 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 refinements comprised a total of seven peaks (of occupancy ca. 50%) assigned to a badly disordered Et$_2$O molecule. CCDC 1821203. See http://www.ccdc.cam.ac.uk/structures for crystallographic files in cif format.


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