ChemComm

A new class of single-molecule magnets: mixed-valent $[Mn_{12}O_8Cl_4(O_2CPh)_8(hmp)_6]$

Colette Boskovic,[a] Euan K. Brechin,[a] William E. Streib,[a] Kirsten Folting,[a] David N. Hendrickson*[b] and George Christou*[a]

[a] *Department of Chemistry and the Molecular Structure Center, Indiana University, Bloomington, IN 47405-7102, USA. E-mail: christou@indiana.edu*

[b] *Department of Chemistry-0358, University of California at San Diego, La Jolla, CA 92093-0358, USA. E-mail: dhendrickson@ucsd.edu*

Received (in Cambridge, UK) 15th December 2000, Accepted 12th January 2001
First published as an Advance Article on the web 19th February 2001

The reaction of $(NBu^n_4)[Mn_8O_6Cl_6(O_2CPh)_7(H_2O)_2]$ with 2-(hydroxymethyl)pyridine (hmpH) or 2-(hydroxyethyl)pyridine (hepH) gives the $Mn^{II}_2Mn^{III}_{10}$ complexes $[Mn_{12}O_8Cl_4(O_2CPh)_8(hxp)_6]$ [$hxp^- = hmp^-$ (1) or hep^- (2)]; these compounds are core isomers with markedly different magnetic properties, compound 1 having an $S = 7$ ground state and displaying strong out-of-phase ac susceptibility signals that establish it as a new class of single-molecule magnet, whereas compound 2 is a low-spin molecule with an $S = 0$ ground state.

In recent years, the search for the ultimate high-density memory devices has afforded so-called single-molecule magnets (SMMs). Each independent molecule in these materials possesses the ability to function as a magnetizable magnet below a critical temperature, owing to intrinsic intramolecular properties rather than intermolecular interactions and long-range ordering. Known SMMs include $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_x]^{n-}$ ($n = 0$–2),[1–4] complexes with the $[Mn^{IV}Mn^{III}_4O_3X]^{6+}$ core,[5] $[Mn_4(O_2CMe)_2(Hpdm)_6]^{2+}$ salts (pdm = anion of pyridine-2,6-dimethanol),[6] $[Fe_8O_2(OH)_{12}(tacn)_6]^{8+}$ salts (tacn = 1,4,7-triazacyclononane),[7] $[Fe_4(OMe)_6(dpm)_6]$ (dpmH = dipivaloylmethane)[8] and $[V_4O_2(O_2CR)_7(L\text{–}L)]^z$ (L–L = 2,2′-bipyridine, pyridine-2-carboxylate anion).[9] A convenient way to detect the slow magnetic relaxation of SMMs is by the appearance of an out-of-phase signal (χ_M'') in ac susceptibility studies, which indicates that the rate of relaxation is insufficient to keep up with the oscillating applied field. We herein report a new class of dodecanuclear Mn-based SMMs with an $S = 7$ ground state and a strong χ'' signal, which occurs at temperatures higher than those observed for all previously reported SMMs, except the $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_x]^{n-}$ family. We also report a structurally related species, whose structural differences result in a low-spin ground state.

Treatment of $(NBu^n_4)[Mn_8O_6Cl_6(O_2CPh)_7(H_2O)_2]$[10] with 4 equivalents of 2-(hydroxymethyl)pyridine (hmpH) or 2-(hydroxyethyl)pyridine (hepH) in MeCN leads to a precipitate after several days. Extraction of the soluble component into CH_2Cl_2 and diffusion of Et_2O into the resulting solution results in crystalline $[Mn_{12}O_8Cl_4(O_2CPh)_8(hxp)_6]$, where $hxp^- = hmp^-$ (**1**) or hep^- (**2**), in yields of $\leqslant$15%.

The centrosymmetric structures of **1** and **2**†‡ (Figs. 1 and 2) each consist of an $[Mn^{III}_{10}Mn^{II}_2(\mu_4\text{-}O)_4(\mu_3\text{-}O)_4(\mu_2\text{-}O)_8(\mu_3\text{-}Cl)_2]$ core, with peripheral ligation provided by six hmp^- (**1**) or hep^- (**2**) ligands, eight O_2CPh^- ligands and two terminal Cl^- ligands. The cores are isomers and can be described as three pairs of face-sharing cuboidal units, (*i.e.* incomplete face-sharing double cubanes). The difference between the cores arises from the manner in which these three units are linked together; the orientation of the 'middle' unit of one compound is related to that of the other by a 120° rotation. Bond valence sums indicate that the two Mn^{II} atoms of each cluster are Mn(6) and Mn(6′). As expected, the ten Mn^{III} atoms in each cluster display a Jahn–Teller elongation. For each cluster, the hxp^- ligands chelate and bridge the Mn atoms of the 'end' units, while the O_2CPh^- groups bridge Mn atoms in the 'middle' unit with those in the 'end' units. However, the arrangement of the peripheral ligands differs between **1** and **2**.

Solid-state dc magnetization measurements were performed on **1** in the range 1.8–300 K in a field of 10.0 kG. The $\chi_M T$ value of 36.6 cm^3 mol^{-1} K at 300 K remains approximately constant as the temperature is decreased until *ca.* 100 K when it begins to increase to a maximum value of 38.3 cm^3 mol^{-1} K at 50 K before rapidly decreasing to 5.3 cm^3 mol^{-1} K at 1.8 K. The spin-only ($g = 2$) value for a unit composed of non-interacting $Mn^{II}_2Mn^{III}_{10}$ ions is 38.8 cm^3 mol^{-1} K. Hence, the molecule appears to have 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 1.8–4.0 K and 1–70 kG. The data were fit using a full-matrix diagonalization approach; the best fits were with $S = 6$, $g = 2.09$, $D \approx -0.8$ cm^{-1} and $S = 7$, $g = 1.79$, $D \approx -0.6$ cm^{-1}, which were of comparable quality but poorer than those normally obtained. This is a common problem in higher nuclearity Mn_x systems[11,12] and is assignable to relatively low-lying excited states, particularly when Mn^{II} ions are present since these typically give weak exchange interactions. We conclude that the molecule has $S = 6$ or 7, although we favour the latter given that $g < 2$.

Ac magnetization measurements were performed on **1** in the 1.8–10 K range in a 3.5 G ac field oscillating at 50–1500 Hz.

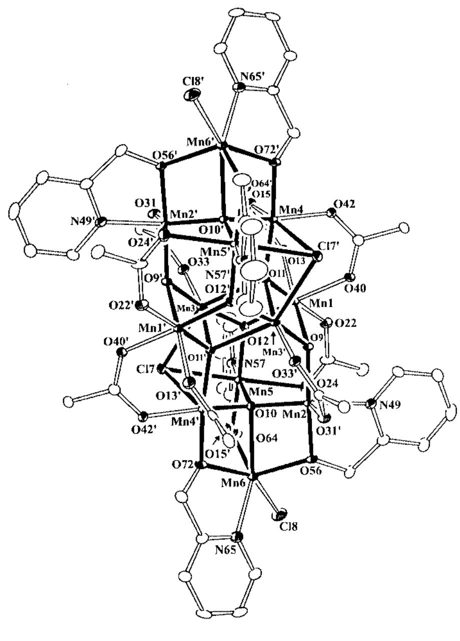

Fig. 1 ORTEP representation of complex **1** at the 50% probability level. For clarity, only the *ipso* carbon atom of each phenyl ring is included.

DOI: 10.1039/b010038m

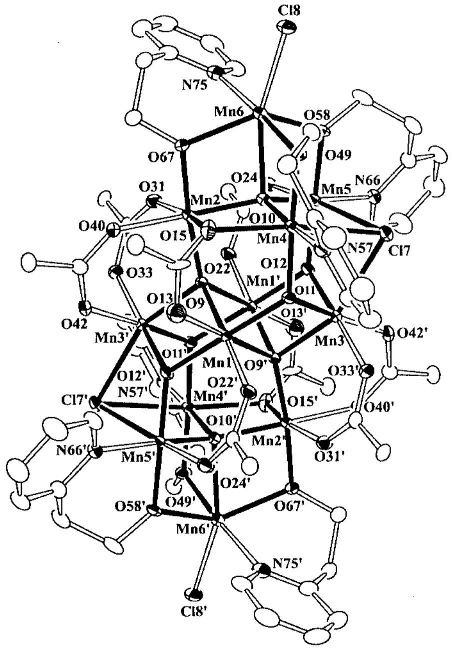

Fig. 2 ORTEP representation of complex **2** at the 50% probability level. For clarity, only the *ipso* carbon atom of each phenyl ring is included.

The in-phase $\chi_M'T$ signal (Fig. 3) shows a frequency dependent decrease at $T < 4$ K, indicative of the onset of slow relaxation on the ms timescale diagnostic of a SMM. This was confirmed by the concomitant appearance of an out-of-phase (χ_M'') signal due to the inability of **1** to relax sufficiently rapidly at these temperatures to keep up with the oscillating field. The χ_M'' signal has a peak at *ca.* 2.75 K at a 997 Hz ac frequency, where the position of the peak corresponds to the temperature at which the relaxation rate is equal to the ac oscillation frequency. Data obtained by varying the frequency of oscillation of the ac field was fit to the Arrhenius equation to obtain the energy barrier (U_{eff}) for the relaxation of the magnetization. The slope of the Arrhenius plot (Fig. 4) gave a U_{eff} of 30.3 K (21.1 cm^{-1}). For an integer spin system, the barrier to thermally activated magnetic relaxation is $S^2|D|$. Thus the experimentally determined kinetic energy barrier of 30.3 K (21.1 cm^{-1}) implies a minimum value of D of -0.62 K (-0.43 cm^{-1}), assuming that $S = 7$. High-field EPR studies will be performed to obtain a more precise value of D.

Solid-state dc magnetization measurements were performed on **2** in the range 1.8–300 K in a 10.0 kG field. The χ_MT value increases slightly from 37.9 cm^3 mol^{-1} K at 300 K to 38.5 cm^3 mol^{-1} K at 200 K before steadily decreasing to 1.5 cm^3 mol^{-1} K at 1.8 K, indicating a low ground state spin value. Ac susceptibility measurements were performed with a 3.5 G ac field oscillating at 997 Hz. The ac and dc data are essentially superimposable (not shown) except at the lowest temperatures and appear to be heading for $\chi_MT = 0$ cm^3 mol^{-1} K at 0 K, suggesting an $S = 0$ ground state. Its very different S value compared with **1** must clearly be due to the core isomerism, which will affect many of the Mn_2 pairwise exchange interactions in the core. No χ_M'' signal is observed for **2** and thus it is not a SMM. In contrast, the structurally related complex **1** displays strong out-of-phase signals in ac susceptibity studies that firmly establish it as a new class of SMM. These signals for **1** occur at relatively high temperatures reflecting the relatively large value of U_{eff}. Indeed, only $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]^{n-}$ complexes have exhibited greater U_{eff} values (Mn_{12} 70 K, $[Mn_{12}]^-$ 55 K, $[Mn_{12}]^{2-}$ 40 K). Thus, the new Mn_{12} complex **1** represents an important new member of the SMM family, and studies of magnetization hysteresis and quantum tunneling of magnetization in this molecule are in progress.

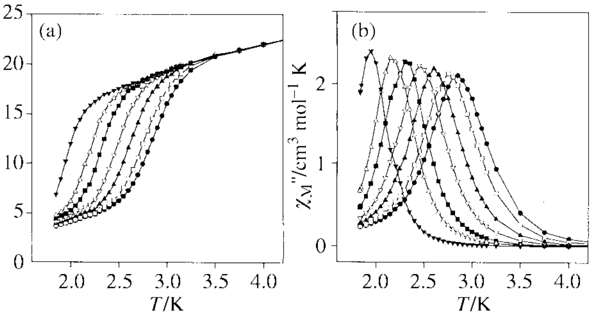

Fig. 3 Plots of (a) the in-phase (χ_M') signal as $\chi_M'T$ and (b) out-of-phase (χ_M'') signal in ac susceptibility studies *vs.* temperature of complex **1** in a 3.5 G field oscillating at 1488 (●), 997 (□), 499 (▲), 250 (▽), 100 (■), 50 (△) and 10 Hz (▼).

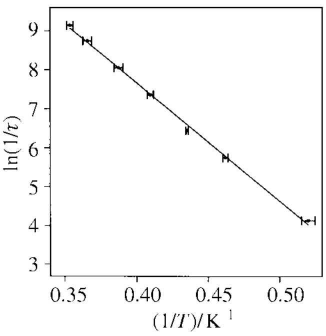

Fig. 4 Arrhenius plot with error bars for complex **1**. The solid line is a fit of the data (see text).

This work was supported by the National Science Foundation.

Notes and references

† The complexes analyzed satisfactorily (C, H, N) as solvent-free. Crystals were kept in contact with the mother liquor to avoid solvent loss and were crystallographically identified as $\mathbf{1}\cdot 2Et_2O\cdot 4CH_2Cl_2$ and $\mathbf{2}\cdot 7CH_2Cl_2$.

‡ *Crystal data:* **1**: $C_{104}H_{104}N_6O_{32}Cl_{12}Mn_{12}$ (including solvate molecules), $M_r = 3034.68$, triclinic, space group $P1$, $a = 14.2602(12)$, $b = 14.8241(12)$, $c = 15.7931(14)$ Å, $\alpha = 15.7931(14)$, $\beta = 94.5578(22)$, $\gamma = 94.5578(22)$°, $U = 3005.87$ Å^3, $Z = 1$, $T = -160$ °C. Residuals R and R_w were 0.0623 and 0.0698, respectively, from refinement on F using 9578 unique data with $F > 2\sigma(F)$. **2**: $C_{105}H_{102}N_6O_{30}Cl_{18}Mn_{12}$ (including solvate molecules), $M_r = 3225.39$, monoclinic, space group $C2/c$, $a = 36.774(3)$, $b = 14.930(1)$, $c = 27.037(3)$ Å, $\beta = 121.884(3)$ °, $U = 312604$ Å^3, $Z = 4$, $T = -168$ °C. Residuals R and R_w were 0.0353 and 0.0379, respectively, from refinement on F using 7908 unique data with $F > 2\sigma(F)$.

CCDC 154915 and 154916. See http://www.rsc.org/suppdata/cc/b0/b010038m/ for crystallographic data in .cif or other electronic format.

1 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.

2 R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, 1993, **365**, 141.

3 H. J. Eppley, H.-L Tsai, N. de Vries, K. Folting, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1995, **117**, 301.

4 M. Soler, S. K. Chandra, D. Ruiz, J. C. Huffman, D. N. Hendrickson and G. Christou, *Chem. Commun.*, 2000, 2417.

5 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.

6 J. Yoo, E. K. Brechin, A. Yamaguchi, M. Nakano, J. C. Huffman, A. L. Maniero, L.-C Brunel, K. Awaga, H. Ishimoto, G. Christou and D. N. Hendrickson, *Inorg. Chem.*, 2000, **39**, 3615.

7 C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli and D. Gatteschi, *Phys. Rev. Lett.*, 1997, **78**, 4645.

8 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.

9 S. L. Castro, Z. Sun, C. M. Grant, J. C. Bollinger, D. N. Hendrickson and G. Christou, *J. Am. Chem. Soc.*, 1998, **120**, 2997.

10 H.-L Tsai, S. Wang, K. Folting, W. E. Streib, D. N. Hendrickson and G. Christou, *J. Am. Chem. Soc.*, 1995. **117**, 2503.

11 M. Soler, E. Rumberger, K. Folting, D. N. Hendrickson and G. Christou, *Polyhedron*, in press.

12 E. K. Brechin, J. Yoo, D. N. Hendrickson and G. Christou, in preparation.