A new manganese cluster topology capable of yielding high-spin species: mixed-valence $[Mn_7(OH)_3Cl_3(hmp)_9]^{2+}$ with $S \geqslant 10$

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The reaction between $MnCl_2{\cdot}4H_2O$, Hhmp (Hhmp = 2-hydroxymethylpyridine) and NEt_4MnO_4 in MeCN gives $NEt_4[Mn_7(OH)_3Cl_3(hmp)_9]Cl[MnCl_4]$ 1; the 4 Mn^{II}, 3 Mn^{III} cation comprises a Mn_6 hexagon containing a central Mn ion, and it possesses a $S \geqslant 10$ ground state.

The study of molecules possessing unusually large spin values in their ground state is an area of intense current research.[1–6] These efforts are driven by a number of considerations, not least of which is the desire to elucidate the various factors responsible for yielding high-spin molecules. These include the topological arrangement of the paramagnetic ions, the nature (ferro- or antiferro-magnetic) of the inter-ion exchange interactions, and the presence of competing exchange interactions of comparable magnitude.[7] Further, it has recently become apparent that a relatively high ground-state spin value is one of the necessary requirements for molecules to be able to exhibit the new phenomenon of single-molecule magnetism.[1,8,9] The synthesis of new high-spin molecules is thus of interest. However, it is difficult to predict in advance for clusters what kind of topology and structure will lead to a high-spin species and even more difficult to then achieve a deliberate synthesis of such a species. We herein describe a new heptanuclear mixed-valence manganese complex with hmp^- ligation (Hhmp = 2-hydroxymethylpyridine) and a new core topology for Mn_7 species, and show that this topology yields a high-spin ground state. Further, we show that these results suggest means whereby additional high-spin molecules might be accessed by small changes to currently available species containing a hexagon of metal ions.

Treatment of a stirred yellow slurry of $MnCl_2{\cdot}4H_2O$ (3 equiv.) and Hhmp (10 equiv.) in MeCN with solid NEt_4MnO_4 (2 equiv.) resulted in a dark brown solution. After 1 h, the solvent was removed *in vacuo* and the residue recrystallized twice (or more) from CH_2Cl_2–Et_2O to give dark brown crystals of $NEt_4[Mn_7(OH)_3Cl_3(hmp)_9]Cl[MnCl_4]$ **1** in typical yields of *ca.* 40%; dried solid analyzed as $\mathbf{1}{\cdot}CH_2Cl_2{\cdot}3H_2O$.† The crystallographic sample of $\mathbf{1}{\cdot}3CH_2Cl_2$ was grown from CH_2Cl_2–toluene. The structure‡ of the $[Mn_7(OH)_3Cl_3(hmp)_9]^{2+}$ cation (Fig. 1) consists of a nearly planar Mn_7 unit comprising a central Mn(1) held within a Mn_6 hexagon by three μ_3-OH^- [O(8), O(9), O(10)] and three μ_3-OR [O(29), O(53), O(77)] groups, the latter from three hmp^- chelates. The remaining hmp^- O atoms doubly bridge Mn_2 pairs of the hexagon. Three terminal Cl^- ions complete peripheral ligation. Charge considerations require a 4 Mn^{II}, 3 Mn^{III} mixed-valence description and, on the basis of Mn^{III} Jahn–Teller (JT) distortions and bond valence sum calculations,[10] the Mn^{III} ions are Mn(2), Mn(4) and Mn(6). The JT elongation axes contain O(29), O(53), O(77) and N(14), N(38), N(62). The cation has virtual C_3 symmetry. The Cl^- anion is hydrogen-bonded to the μ_3-OH^- groups [O$\cdots$Cl 3.049(16)–3.187(16) Å], but the NEt_4^+ and $MnCl_4^{2-}$ ions are well separated from the Mn_7 cation. A side view (Fig. 1) shows a Mn/O layered structure, with layers of O atoms above and below the Mn_7 layer, reminiscent of the hexagonal close-packed layered structure in, *e.g.* CdI_2.[11] The structure is different from that of other Mn_7 complexes, but similar to that of $[M_6NaL_{12}]^+$ ($M = Co^{II}$, Cu^{II}; HL = 6-methyl-2-hydroxypyridine)[12] and $[Fe_6Na(OMe)_{12}(dbm)_6]^+$ ($6Fe^{III}$; Hdbm = dibenzoylmethane),[13] where a Na^+ ion occupies the central position, and also $[Cu_7L_{12}]^{2+}$ ($7Cu^{II}$)[14] and $[Fe_7(OMe)_6(OPh)_6(MeCN)_{12}]^{2+}$ ($7Fe^{II}$),[15] which are homometallic.

Magnetic susceptibilities (χ_M) of $\mathbf{1}{\cdot}CH_2Cl_2{\cdot}3H_2O$ have been measured in a 10.0 kG dc field and a 1.0 G ac field oscillating at 1000 Hz and corrected for the presence of the $MnCl_4^{2-}$ ($S = 5/2$) ion, which is assumed, based on the crystal structure, to not be interacting with the Mn_7 cation. The dc χ_mT is essentially temperature independent at *ca.* 26.4 cm^3 K mol^{-1} until *ca.* 100 K, and then increases to a maximum of 27.70 cm^3 K mol^{-1} at 30.0 K and then decreases to 12.28 cm^3 K mol^{-1} at 2.00 K. Similar values are seen for the ac χ_MT data, although it does not decrease as much at low temperatures. The data suggest a large ground-state spin value, and magnetization *vs.*

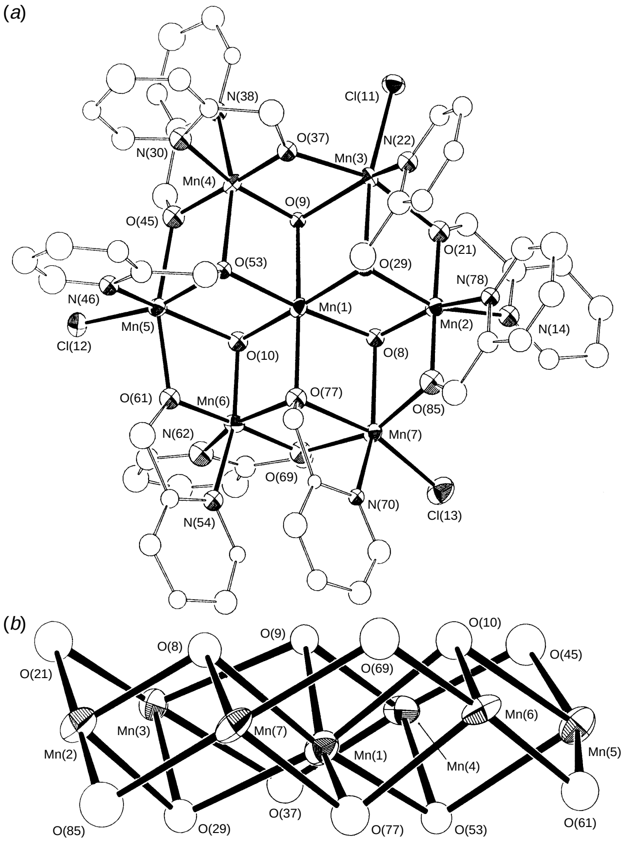

Fig. 1 (*a*) The structure of the $[Mn_7(OH)_3Cl_3(hmp)_9]^{2+}$ cation of **1** viewed approximately along the virtual C_2 axis. Selected distances (Å): Mn(1)$\cdots$Mn(2) 3.196(6), Mn(1)$\cdots$Mn(3) 3.376(5), Mn(1)$\cdots$Mn(4) 3.184(5), Mn(1)$\cdots$Mn(5) 3.353(6), Mn(1)$\cdots$Mn(6) 3.180(5), Mn(1)$\cdots$Mn(7) 3.362(5), Mn(2)$\cdots$Mn(3) 3.291(5), Mn(3)$\cdots$Mn(4) 3.232(5), Mn(4)$\cdots$Mn(5) 3.297(5), Mn(5)$\cdots$Mn(6) 3.202(5), Mn(6)$\cdots$Mn(7) 3.295(5), Mn(2)$\cdots$Mn(7) 3.234(5). (*b*) A side view emphasizing the O/Mn/O layers. Displacement of Mn(1) from the Mn_6 least-squares plane is 0.388 Å.

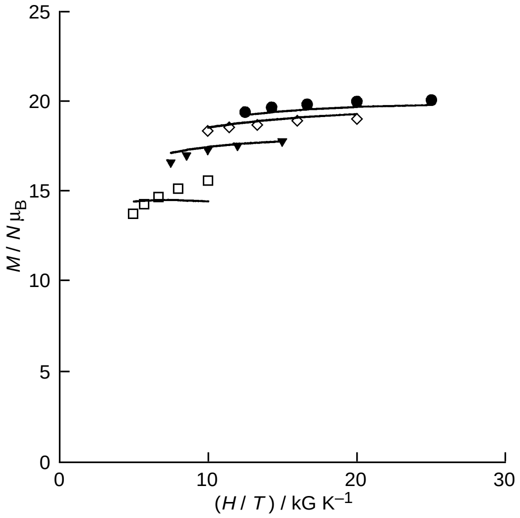

Fig. 2 Reduced magnetization ($M/N\mu_B$) *vs.* H/T data for complex **1**. The solid lines are the fit to a $S = 11$ state with $g = 1.85$ and $D = -0.15$ cm^{-1}.

field data were therefore collected in the 20–50 kG and 2.00–4.00 K ranges (Fig. 2). Fitting of these data, employing a spin-Hamiltonian matrix diagonalization approach, gave $S = 11$, $g = 1.85$ and $D = -0.15$ cm^{-1}; an equally good fit was obtained with $S = 10$, $g = 2.03$ and $D = -0.18$ cm^{-1}, which, however, is slightly less favored by the $g > 2$ value. Attempts to fit magnetization data measured at temperatures above *ca.* 4 K resulted in poor fits assuming only one state is populated. We conclude that in the 2–4 K range, the lowest energy state in a 20–50 kG field has $S = 11$. At temperatures above *ca.* 4 K, other states with smaller S values are presumably populated and this is why the maximum in $\chi_M T$ at *ca.* 30 K falls short of the value expected for a molecule with $S = 10$ or 11; weak, intermolecular antiferromagnetic exchange interactions likely also serve to decrease the $\chi_M T$ value at low temperature. No out-of-phase ac signals were observed in the ac studies in the 2.00–50 K range.

A ground-state spin value for **1** of $S \geqslant 10$ makes this complex a new member of the small family of high-spin ($S \geqslant 8$) complexes.[1–8] With 4 Mn^{II} and 3 Mn^{III} ions, **1** could have ground-state values in the range $S = 2$–16. The intermediate value of $S \geqslant 10$ can be rationalized as due to competing exchange interactions of comparable magnitude.[7] The pairwise exchange interactions are of two types: J_{io} and J_{oo} (i = inner, o = outer), the former comprising both J_{22} (Mn^{II}–Mn^{II}) and J_{23} (Mn^{II}–Mn^{III}) interactions and the latter only J_{23}. The ground state of **1** will be dependent on the relative magnitudes of the competing J_{io} and J_{oo} interactions, since literature precedent indicates that J_{22} and J_{23} interactions are essentially always weakly antiferromagnetic and of comparable magnitude.[16] Thus, as a result of the J_{io} *vs.* J_{oo} competition, it is impossible for the spins in **1** to align antiparallel to each of their neighboring spins and the ground state consequently adopts an intermediate spin value, one of the highest yet observed.

The above analysis predicts that if the central Mn(1) ion of **1** were missing (or replaced by, *e.g.* Na$^+$), there would be no competing exchange interactions and the ground state would be $S = 15/2 - 6 = 3/2$. These species are currently not known and are being sought to test this prediction, but we note that [Fe$_6$Na(OMe)$_{12}$(dbm)$_6$]$^+$ (6 Fe^{III}) has an $S = 0$ ground state[13] consistent with antiparallel alignments of six $S = 5/2$ spins around the ring. Replacement of the Na$^+$ in this complex with a seventh Fe^{III} or any other paramagnetic ion should give relatively high ground-state spin values as competing exchange interactions are introduced. This introduction of a seventh paramagnetic centre into preformed M$_6$Na (or M$_6$) species may or may not prove synthetically challenging; however, challenging or not, it certainly warrants investigation since success would be extremely beneficial for the future health of the field of high-spin molecules, which is currently heavily dependent on serendipity. We also note that exactly the above kind of Fe$^{III}{}_7$ unit {*i.e.* [Fe$_7$(μ_3-OH)$_6$(μ_2-OH)$_6$]$^{9+}$} is a recognizable fragment within the cores of cocrystallized [Fe$_{17}$O$_4$(OH)$_{16}$(heidi)$_8$(H$_2$O)$_{12}$](NO$_3$)$_3$/[Fe$_{19}$O$_6$(OH)$_{14}$(heidi)$_{10}$(H$_2$O)$_{12}$](NO$_3$) [heidi = N(CH$_2$CO$_2$H)$_2$(CH$_2$CH$_2$OH)] and is undoubtedly a major contributor to the S *ca.* 33/2 ground state of one of them.[2]

Note added in proof: the related cation [Zn$_7$(hmp)$_{12}$]$^{2+}$ has very recently been reported.[17]

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Footnotes and References

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† The complex analysed satisfactorily (C, H, N, Cl) as **1**·CH$_2$Cl$_2$·3H$_2$O.

‡ *Crystal data*: **1**·3CH$_2$Cl$_2$, triclinic, space group $P\bar{1}$, $a = 17.592(6)$, $b = 19.393(6)$, $c = 12.735(3)$ Å, $\alpha = 95.99(2)$, $\beta = 95.72(1)$, $\gamma = 82.89(1)$°, $U = 4271$ Å^3, $Z = 2$, $T = -153$ °C, $\mu = 15.985$ cm^{-1}, $D_c = 1.658$ g cm^{-3}. The structure was solved using MULTAN-78 and refined on F to $R(F) = 0.0936$ and $R_w(F) = 0.0891$ using 4183 unique reflections with $F > 2.33\sigma(F)$. CCDC 182/512.

1 H. J. Eppley, H.-L. Tsai, N. de Vries, K. Folting, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1995, **117**, 301; H.-L. Tsai, S. Wang, K. Folting, W. E. Streib, D. N. Hendrickson and G. Christou, *J. Am. Chem. Soc.*, 1995, **117**, 2503; H. J. Eppley, S. Wang, H.-L. Tsai, S. M. Aubin, K. Folting, W. E. Streib, D. N. Hendrickson and G. Christou, *Mol. Cryst. Liq. Cryst.*, 1995, **274**, 159.

2 A. K. Powell, S. L. Heath, D. Gatteschi, L. Pardi, R. Sessoli, G. Spina, F. Del Giallo and F. Pieralli, *J. Am. Chem. Soc.*, 1995, **117**, 2491.

3 A. Scuiller, T. Mallah, M. Verdaguer, A. Nivorozkhin, J.-L. Tholence and P. Veillet, *New J. Chem.*, 1996, **20**, 1.

4 C. D. Delfs, D. Gatteschi, L. Pardi, R. Sessoli, K. Weighardt and D. Hanke, *Inorg. Chem.*, 1993, **32**, 3099; A. Caneschi, D. Gatteschi, J. Laugier, P. Rey, R. Sessoli and C. Zanchini, *J. Am. Chem. Soc.*, 1988, **110**, 2795.

5 D. P. Goldberg, A. Caneschi, C. D. Delfs, R. Sessoli and S. J. Lippard, *J. Am. Chem. Soc.*, 1995, **117**, 5789.

6 A. J. Blake, C. M. Grant, S. Parsons, J. M. Rawson and R. E. P. Winpenny, *J. Chem. Soc., Chem. Commun.*, 1994, 2363.

7 D. N. Hendrickson in *Research Frontiers in Magnetochemistry*, ed. C. J. O'Connor, World Scientific, Singapore, 1993.

8 R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, 1993, **365**, 141; D. Gatteschi, A. Caneschi, L. Pardi and R. Sessoli, *Science*, 1994, **265**, 1054.

9 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.

10 I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B*, 1985, **41**, 244.

11 *Inorganic Structural Chemistry*, ed. U. Muller, Wiley, New York, 1993.

12 S. McConnell, M. Motevalli and P. Thornton, *Polyhedron*, 1995, **14**, 459; A. J. Blake, R. O. Gould, P. E. Y. Milne and R. E. P. Winpenny, *J. Chem. Soc., Chem. Commun.*, 1991, 1453.

13 A. Caneschi, A. Cornia and S. J. Lippard, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 467.

14 A. J. Blake, R. O. Gould, C. M. Grant, P. E. Y. Milne, D. Reed and R. E. P. Winpenny, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 195.

15 V. S. Nair, A. Kitaygorodskiy and K. S. Hagen, *Abstracts of Papers, 206th National Meeting of the American Chemical Society*, Washington, DC, 1993, INOR 525.

16 L. Que, Jr. and A. E. True, *Prog. Inorg. Chem.*, 1990, **38**, 97.

17 M. Tesmer, B. Muller and H. Vahrenkamp, *Chem. Commun.*, 1997, 721.

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