

## A Decanuclear Mixed-Valent Manganese Complex with a High Spin Multiplicity in the Ground State

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Recent advances in the production of “nanostructured materials” by condensed-matter scientists have afforded substances with some spectacular magnetic properties arising from quantum effects.<sup>1–3</sup> The solid-state physicist relies on methods for dividing bulk magnetic materials into their component nanometer-sized particles while trying to maintain control over their size, shape, and crystal structures. The synthetic chemist approaches the problem from the other direction, by attempting to build up well-defined small molecules having large numbers of unpaired spins. By incorporating units of unpaired spin, such as nitrenes and carbenes, into the appropriate  $\pi$ -conjugated framework, the necessary magnetic coupling can be achieved to yield organic molecules with high-spin ground states.<sup>4–6</sup>

Inorganic chemists have similarly been able to assemble polynuclear clusters with high-spin ground states arising from magnetic superexchange interactions among transition-metal centers.<sup>7–14</sup> Two long-term goals in the search for such high-nuclearity spin clusters are to obtain molecules with a spin multiplicity high enough to observe intercluster magnetic ordering in the solid state and to prepare nanosized complexes which themselves constitute a single magnetic domain.<sup>10,11,13</sup> In pursuit of the latter objective, we have synthesized and determined the structural and magnetic properties of  $(\text{Me}_4\text{N})_4[\text{Mn}_{10}(\text{biphen})_4\text{O}_4\text{Cl}_{12}]$  (biphen = 2,2'-biphenoxide), which exhibits the highest spin ground state known for a discrete compound. The structural analysis reveals the anion **1** to be a highly symmetric (idealized point group  $D_{2d}$ ), mixed-valent  $\text{Mn}(\text{II})_6\text{Mn}(\text{III})_4$  complex. The geometric motif exhibited by **1** is unknown in manganese or related polyiron oxo cluster compounds,<sup>15–24</sup> and **1** is a rare example of

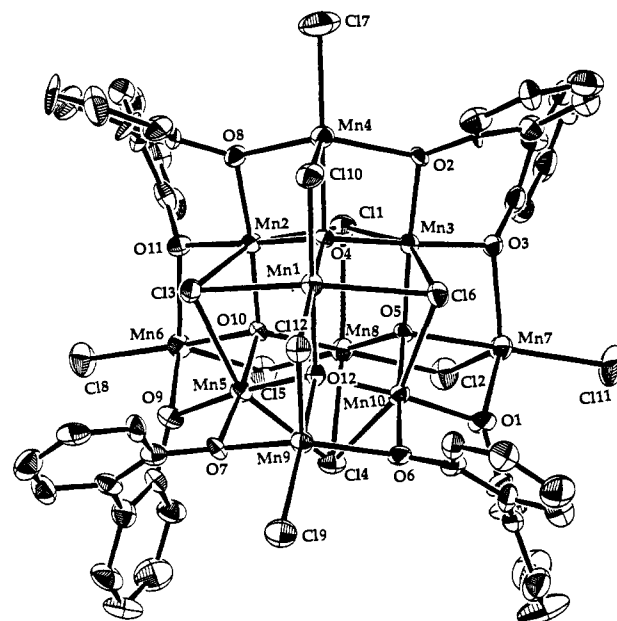


Figure 1. ORTEP diagram of **1** showing the 50% probability thermal ellipsoids. Hydrogen atoms were omitted for clarity.

a polynuclear manganese complex held together without carboxylate bridges.<sup>25,26</sup> The synthesis of the bromide analogue  $[\text{Mn}_{10}(\text{biphen})_4\text{O}_4\text{Br}_{12}]^{4-}$  (**2**) and a comparison of its magnetic properties with those of **1** are also presented.

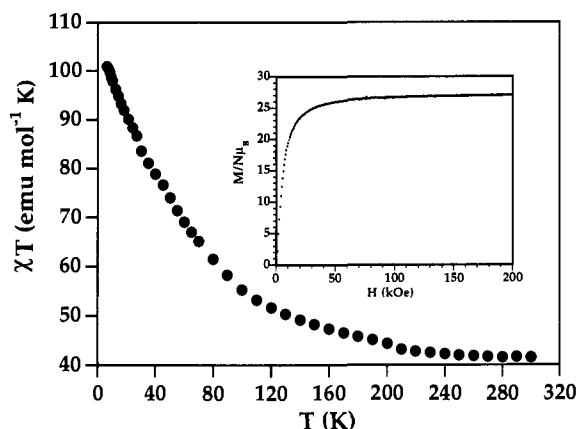
Addition of  $\text{Me}_4\text{N}(\text{OH})\cdot 5\text{H}_2\text{O}$  (0.50 mmol) to a solution of  $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$  (2.54 mmol) and 2,2'-biphenol (5.40 mmol) in ethanol resulted in a dark red-brown reaction mixture, from which X-ray quality black crystals of  $(\text{Me}_4\text{N})_4[\text{Mn}_{10}(\text{biphen})_4\text{O}_4\text{Cl}_{12}]$  were obtained in less than 1% yield after filtration and layering with  $\text{C}_6\text{H}_6$ .<sup>27</sup> This low yield method provided the sample studied by X-ray diffraction. Synthesis of analytically pure **1** on a larger scale was accomplished by vapor diffusion or layering of  $\text{CH}_2\text{Cl}_2$  with the EtOH reaction mixture, which afforded  $(\text{Me}_4\text{N})_4\cdot 1$  as black crystals in 50-mg quantities (15–20% yield).<sup>28</sup> Magnetic studies were performed on material obtained in this manner. Preparation of the bromide derivative  $(\text{Me}_4\text{N})_4\cdot 2$ <sup>29</sup> was accomplished by an analogous procedure in which  $\text{MnBr}_2\cdot 4\text{H}_2\text{O}$  was substituted for  $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ .

The structure of **1** is shown in Figure 1. The core of the cluster is comprised of a  $\text{Mn}_6\text{O}_4$  adamantyl-type framework. A six-membered ring formed by Mn(5), O(10), Mn(8), O(5), Mn(10),

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- (27) Crystal data for  $(\text{Me}_4\text{N})_4\cdot 1\cdot 3\text{C}_6\text{H}_6\cdot 2\text{EtOH}\cdot 5\text{biphenH}_2$  at 195 K: size ca.  $0.2 \times 0.2 \times 0.4$  mm, monoclinic, space group  $P2_1/n$  (No. 14),  $a = 20.151(4)$  Å,  $b = 18.189(2)$  Å,  $c = 30.415(7)$  Å,  $\beta = 97.44(1)^\circ$ ;  $V = 11054(4)$  Å<sup>3</sup>,  $Z = 4$ . For 8894 unique, observed reflections with  $F^2 > 3\sigma(F^2)$  and 472 variable parameters, the current discrepancy indices are  $R = 0.077$  and  $R_w = 0.104$ .
- (28) The crystalline material of  $(\text{Me}_4\text{N})_4\cdot 1$  was isolated by filtration, crushed, and dried in vacuum at 111 °C for 24 h. Anal. Calcd for  $\text{C}_{64}\text{H}_{80}\text{N}_4\text{Cl}_{12}\text{O}_{12}\text{Mn}_{10}$ : C, 37.10; H, 3.89; N, 2.70. Found: C, 36.86; H, 3.85; N, 2.57. The drying step was necessary because of the large amount of methylene chloride contained in the crystal lattice. If the crystals were allowed to stand in the air for several days, a satisfactory analysis was obtained for  $(\text{Me}_4\text{N})_4\cdot 1\cdot \text{CH}_2\text{Cl}_2$ . Anal. Calcd for  $\text{C}_{65}\text{H}_{82}\text{N}_4\text{Cl}_{14}\text{O}_{12}\text{Mn}_{10}$ : C, 36.19; H, 3.83; N, 2.60. Found: C, 35.95; H, 3.80; N, 2.54. Magnetic behavior was essentially the same for either the solvated or the nonsolvated form.
- (29) Anal. Calcd for  $\text{C}_{64}\text{H}_{80}\text{N}_4\text{Br}_{12}\text{O}_{12}\text{Mn}_{10}$ : C, 29.50; H, 3.09; N, 2.15. Found: C, 29.21; H, 2.95; N, 1.99.



**Figure 2.** Plot of the temperature dependence of the molar paramagnetic susceptibility times temperature,  $\chi T$ , for a polycrystalline sample of  $(\text{Me}_4\text{N})_4\cdot\mathbf{1}$ . The theoretical value of  $\chi T$  for the 10 independent manganese ions in  $\mathbf{1}$  is  $38.2 \text{ emu mol}^{-1} \text{ K}$ , assuming  $g = 2.00$ . The inset shows a plot of reduced magnetization,  $M/N\mu_B$ , where  $N$  is Avogadro's number and  $\mu_B$  is the Bohr magneton, versus field at 4.2 K.

and O(12) is linked by its three  $\mu_4$ -oxo ligands to octahedral Mn(1), Mn(2), and Mn(3) ions, which in turn are connected by the bridgehead oxygen atom O(4). Each of the four  $\mu_4$ -oxo ligands is bonded to an additional, trigonal-bipyramidal Mn ion located on the cluster periphery. The four biphenoxide ligands are each chelated to one Mn(III) ion, distinguishing these higher oxidation state centers (vide infra) from the remaining Mn(II) ions. The oxygen donors from each biphenoxide ligand also form bridges to neighboring Mn ions in the cluster, resulting in four linear arrays comprised of a central Mn(III) and two trigonal-bipyramidal Mn(II) ions. The cluster is completed by 12 chloride ligands, which have three distinct bonding modes. Each of the four chloride ions Cl(3), Cl(6), Cl(4), and Cl(1) bridges three of the manganese ions located in the central adamantane framework. Two other linearly disposed sets of three manganese atoms, Mn(9), Mn(1), Mn(4), and Mn(6), Mn(8), Mn(7), are bridged by four  $\mu_2$ -chloride ligands down the front spine and along the back edge of the complex, respectively. The remaining four terminal chlorides complete the coordination sphere of the pentacoordinate Mn(II) ions.

Oxidation states for the manganese ions were assigned on the basis of overall charge considerations and an examination of the relative bond lengths for the different metal sites. The average Mn–O distance for the four Mn(III) ions, which are located in a  $\text{Cl}_2\text{O}_4$  environment, is  $1.90 \text{ \AA}$ . This value is considerably shorter than the distance for the four Mn(II) ions Mn(4), Mn(6), Mn(9), and Mn(7) in a  $\text{Cl}_2\text{O}_3$  environment, for which  $\text{Mn–O}_{\text{av}} = 2.18 \text{ \AA}$ , or the two Mn(II) atoms Mn(1) and Mn(8) in  $\text{Cl}_4\text{O}_2$  sites, which have  $\text{Mn–O}_{\text{av}} = 2.14 \text{ \AA}$ . Each of the four Mn(III) ions exhibits a marked axial elongation, resulting in an average Mn–Cl distance of  $2.71 \text{ \AA}$ , which may be attributed to a Jahn–Teller effect. From this geometric information, we assign a total of six Mn(II) and four Mn(III) ions to the cluster, giving an overall charge of  $24+$  for the metal ions. The ligands ( $4\text{biphen}^{2-} + 4\text{O}^{2-} + 12\text{Cl}^-$ ) give a total charge of  $28-$ , resulting in a  $4-$  charge for  $\mathbf{1}$ , which is balanced by the four  $\text{Me}_4\text{N}^+$  cations. Oxidation state assignments are thus corroborated by the charge balance.

Figure 2 shows the magnetic properties of  $\mathbf{1}$  measured in an external magnetic field of  $3000 \text{ Oe}$ .<sup>30</sup> Ten magnetically non-interacting manganese ions in a  $\text{Mn(II)}_6\text{Mn(III)}_4$  cluster with  $g = 2$  would give rise to a  $\chi T$  value of  $38.2 \text{ emu mol}^{-1} \text{ K}$ , which

(30) Magnetic measurements were performed on a Quantum Design MPMS SQUID susceptometer maintained by the Center for Materials Science and Engineering at M.I.T. The data were corrected for the diamagnetic contribution of the sample holder, and Pascal's constants were used to calculate the diamagnetic correction for the complexes.

approaches the observed value of  $41.5 \text{ emu mol}^{-1} \text{ K}$  at  $300 \text{ K}$ . As the temperature is lowered,  $\chi T$  increases steadily, reaching a maximum  $101 \text{ emu mol}^{-1} \text{ K}$  at  $6 \text{ K}$ .<sup>31</sup> The magnetic behavior for the bromo analogue  $\mathbf{2}$  was found to be essentially the same.<sup>32</sup>

The low-temperature magnetic data are consistent with a population of spin states  $S = 13$  and  $S = 14$ , since the theoretical  $\chi T$  value for  $S = 14$  and  $g = 2.00$  is  $105 \text{ emu mol}^{-1} \text{ K}$ . The magnetization of  $\mathbf{1}$  was measured at  $4.2 \text{ K}$  as a function of the applied field up to a maximum value of  $200 \text{ kOe}$ .<sup>33</sup> At low field, a rapid increase in magnetization was observed which reached a final saturation value of  $27.1 \mu_B$  in the high-field region, as shown in the inset of Figure 2. For the bromo analogue  $\mathbf{2}$ , the shape of the magnetization versus field curve was the same as that for  $\mathbf{1}$ , and a final saturation value of  $28.3 \mu_B$  was obtained. These values correspond, within the experimental limit and assuming  $g = 2.00$ , to a mostly populated  $S = 14$  state. To our knowledge,  $\mathbf{1}$  has the highest spin multiplicity reported thus far for a discrete molecule. The previous record,  $S = 12$ , was observed for an  $\text{Mn}_6$  nitronyl nitroxide ring compound.<sup>8</sup>

In other polynuclear manganese clusters containing  $\mu_4$ -oxo bridges, antiferromagnetic interactions are observed.<sup>34–36</sup> The multiple exchange pathways and high symmetry of  $\mathbf{1}$  may give rise to a large amount of spin frustration, causing the multiplicity of the ground state to assume an intermediate value between that of a simple antiferromagnetic system with  $S = 0$  and that of a completely ferromagnetically coupled complex. If all the ions were ferromagnetically coupled, one would expect an  $S = 23$  ground state, for which, assuming  $g = 2.00$ ,  $\chi T$  would be  $276 \text{ emu mol}^{-1} \text{ K}$  at low temperature, considerably higher than the observed value for  $\mathbf{1}$ .

A complete understanding of the magnetostructural relationships for the present and related polynuclear metal clusters will require considerable theoretical effort. Linkage of these clusters through ligand bridges that allow for intermolecular magnetic exchange is an attractive synthetic goal in view of the interest in developing extended ferromagnetic materials.<sup>37</sup>

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**Supplementary Material Available:** Description of methods of data collection and tables of atomic positional and thermal parameters for  $(\text{Me}_4\text{N})_4[\text{Mn}_{10}(\text{biphen})_4\text{O}_4\text{Cl}_{12}]\cdot 3\text{C}_6\text{H}_6\cdot 2\text{EtOH}\cdot 0.5\text{biphenH}_2$  (18 pages). Ordering information is given on any current masthead page.

(31) Such a remarkably high  $\chi T$  value led us to check whether the sample might be comprised of microcrystallites mechanically reorienting with the applied field. Measurements were therefore repeated for  $\mathbf{1}$  at  $100 \text{ Oe}$  and showed essentially the same magnetic behavior, confirming that no reorientation was taking place during the SQUID measurement. In an initial report on the magnetochemistry of the polynuclear manganese cluster  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CPh})_{16}(\text{H}_2\text{O})_4]$ , a ground state of  $S = 14$  was assigned, (Boyd, P. D. W., et al. *J. Am. Chem. Soc.* **1988**, *110*, 8537–8539), but a more detailed analysis revealed this assignment to be incorrect due to the torquing of the crystallites in the applied field. Ground states of  $S = 9$  for this  $\text{Mn}_{12}$  complex and  $S = 10$  for an acetate derivative were later determined.<sup>13</sup>

(32) For a recent example of a comparison of the magnetic properties of the Cl<sup>−</sup> and Br<sup>−</sup> analogues of a tetranuclear Mn complex in which the halide is triply bridging, see ref 23 above.

(33) Magnetization experiments were performed at the Francis Bitter National Magnet Laboratory, M.I.T.

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