J. Am. Chem. Soc. **1998,** *120,* 2977−2978

High-Spin Molecules: Hexanuclear $[Mn_6O_4Cl_4(Me_2dbm)_6]$ (Me_2dbmH = 4,4′-Dimethyldibenzoylmethane) with a Near Tetrahedral $[Mn_6O_4Cl_4]^{6+}$ Core and a $S = 12$ Ground State

Guillem Aromí,[1a] Juan-Pablo Claude,[1a,c] Michael J. Knapp,[1b]
John C. Huffman,[1a] David N. Hendrickson,*,[1b] and
George Christou*,[1a]

Department of Chemistry and Molecular
Structure Center, Indiana University
Bloomington, Indiana 47405-4001
Department of Chemistry-0358
University of California at San Diego
La Jolla, California 92093-0358

Received November 24, 1997

An interesting sub-area of transition-metal cluster chemistry is the small but growing family of molecules that, in their ground states, have unusually large numbers of unpaired electrons. Molecular clusters with spin (*S*) values as high as double figures have been discovered, with the highest value to date being $S \approx 16^1/_2$ for one of the clusters in a sample of cocrystallized Fe_{17} and Fe_{19} species,[2] but examples with $S \geq 8$ are nevertheless very rare.[3,4] The study of such molecules has shown that the high spin value is a result of the presence of (at least some) ferromagnetic exchange interactions between the metal ions and/or spin frustration effects arising from the presence in certain M_x topologies of competing exchange interactions which prevent (frustrate) the preferred spin alignments that would otherwise normally yield low-spin species.

The study of high-spin molecules has taken on additional importance in recent years as it has been realized that a fairly large *S* value is a necessary (but not sufficient) property for molecules to exhibit the new magnetic phenomenon of single-molecule magnetism, i.e., the ability of material composed of discrete, (magnetically) noninteracting molecules to be magnetized by an external magnetic field below a critical blocking temperature (T_B).[3a,5,6] The importance of a high *S* value in such nanoscale magnets has stimulated a search for new examples of species with this property. We herein report the preparation of a new hexanuclear Mn^{III} cluster with an aesthetically pleasing $[Mn_6O_4Cl_4]^{6+}$ core and show that it possesses a $S = 12$ ground state, one of the highest yet identified.

Treatment of $[Mn_4O_2(O_2CMe)_6(py)_2(Me_2dbm)_2]$ (**1**) (Me_2dbmH = 4,4′-dimethyldibenzoylmethane), prepared as for the dbm analogue,[7] in CH_2Cl_2 with 6 equiv of Me_3SiCl and 2 equiv of Me_2dbmH gave a brown solution from which was isolated crude $[MnCl(Me_2dbm)_2]$ (**2**) on addition of Et_2O. Redissolution in $MeCN:CH_2Cl_2$ (1:1) followed by standing and slight concentration at room temperature over ∼3 weeks gave black crystals of $[Mn_6O_4Cl_4(Me_2dbm)_6]\cdot 3CH_2Cl_2$ ($\mathbf{3}\cdot 3CH_2Cl_2$), together with some white powder. The latter was removed by filtration and washing of the black crystals with EtOH. Complex **3** can also be obtained by dissolving purified **2** in $MeCN:CH_2Cl_2$ (1:1), and subsequent treatment as above, suggesting the formation of **3** to involve a slow hydrolysis of the mononuclear species.[8] Nonoptimized yields up to 14% have been obtained to date.[8]

The structure[9] of **3** (Figure 1) consists of a $(Mn^{III})_6$ octahedron with four nonadjacent faces bridged by the μ_3-O^{2-} ions and the other four faces by μ_3-Cl^- ions. Six-coordinate, approximately octahedral geometry at each metal is completed by a chelating Me_2dbm group. The cluster has virtual T_d symmetry. As expected for high-spin, octahedral Mn^{III}, there is a Jahn−Teller (JT) distortion, taking the form of an axial elongation of the two trans Mn−Cl bonds, making them unusually long (2.618(3)−2.692(3) Å). In contrast, the $Mn-O^{2-}$ (1.876(4)−1.899(5) Å) and $Mn-O(Me_2dbm)$ (1.903(5)−1.925(5) Å) bond lengths are as expected. As a result of (i) the long $Mn-Cl^-$ versus short $Mn-O^{2-}$ bonds and (ii) the near trigonal planar geometry at the latter (sum-of-angles (soa) ≈ 349°) compared with marked trigonal pyramidal geometry at the former (soa ≈ 223°), the $[Mn_6O_4Cl_4]^{6+}$ core is a near tetrahedron with a Cl^- at each vertex, a Mn at the midpoint of each edge, and a O^{2-} bridging each face. Although many $[M_6(\mu_3\text{-}X)_8]$ face-capped metal octahedra are known,[10] only a relative few contain two types of X group, e.g., the $[Ti_6O_6Cl_2]$,[11] $[Ti_6Te_6O_2]$,[12] and $[Re_6Y_xZ_{8-x}]$ ($x = 5$, Y = S or Se, Z = Cl; $x = 6$, Y = S, Z = Cl)[13] cores. Only the $[Ti_6(\mu_3\text{-}O)_4(\mu_3\text{-}Cl)_4]$ core of $[(C_5H_5Me)_6Ti_6O_4Cl_4]$[11] contains, like **3**, four O^{2-} and 4 Cl^- bridges, but the structure does not approximate to a tetrahedron. $[Mn^{III}{}_6X_8]$ species have been unknown to date, although a $[Mn_6(\mu_3\text{-}O)_4(\mu_3\text{-}Cl)_4]^{4+}$ unit as found in **3** but at the $2Mn^{II}$, $4Mn^{III}$ level is also a recognizable fragment within the higher nuclearity cluster $[Mn_{10}O_4Cl_{12}(biphen)_4]^{4-}$ (biphen = 2,2′-biphenoxide).[14]

---

(1) (a) Indiana University. (b) University of California at San Diego. (c) Present address: Department of Chemistry, University of Alabama at Birmingham.

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

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

(4) (a) Scuiller, A.; Mallah, T.; Verdaguer, M.; Nivorozkhin, A.; Tholence, J.-L.; Veillet, P. *New J. Chem.* **1996**, *20*, 1. (b) Delfs, C. D.; Gatteschi, D.; Pardi, L.; Sessoli, R.; Wieghardt, K.; Hanke, D. *Inorg. Chem.* **1993**, *32*, 3099. (c) Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P.; Sessoli, R.; Zanchini, C. *J. Am. Chem. Soc.* **1988**, *110*, 2795. (d) Goldberg, D. P.; Caneschi, A.; Delfs, C. D.; Sessoli, R.; Lippard, S. J. *J. Am. Chem. Soc.* **1995**, *117*, 5789. (e) Blake, A. J.; Grant, C. M.; Parsons, S.; Rawson, J. M.; Winpenny, R. E. P. *J. Chem. Soc., Chem. Commun.* **1994**, 2363. (f) Bolcar, M. A.; Aubin, S. M. J.; Folting, K.; Hendrickson, D. N.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1997**, 1485. (g) Benelli, C.; Parsons, S.; Solan, G. A.; Winpenny, R. E. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1825

(5) (a) Sessoli, R.; Tsai, H.-L.; Schake, A. R.; Wang, S.; Vincent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 1804. (b) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141.

(6) Aubin, S. M. J.; Wemple, M. W.; Adams, D. M.; Tsai, H.-L.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1996**, *118*, 7746.

(7) Wang, S.; Folting, K.; Streib, W. E.; Schmitt, E. A.; McCusker, J. K.; Hendrickson, D. N.; Christou, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 305.

(8) The reaction is more complicated than this statement suggests, with $[Mn(Me_2dbm)_3]$ identified in the filtrate; the isolation of pure **3** is undoubtedly due to its low solubility in this solvent mixture. Isolated solid is soluble in CH_2Cl_2 and $CHCl_3$. ^1H NMR spectra in these solvents suggest the structure is retained on dissolution.

(9) Dried solid analyzed as $\mathbf{3}\cdot 0.4CH_2Cl_2$. Anal. Calcd (found) for $C_{102.4}H_{90.8}O_{16}Cl_{4.8}Mn_6$: C, 59.21 (59.28); H, 4.49 (4.41). Crystal data for $\mathbf{3}\cdot 3CH_2Cl_2$: monoclinic; $P2_1/c$; $a = 17.172(2)$ Å, $b = 18.302(2)$ Å, $c = 34.534(4)$ Å; $\beta = 100.36(1)°$; $Z = 4$; $V = 10677$ Å^3; $d_{calcd} = 1.430$ g cm^{-3}; $T = -171$ °C. The structure was solved using MULTAN and refined on *F* to $R(R_w) = 5.80$ (5.73) using 9989 unique reflections with $F > 2.33\sigma(F)$. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were included as fixed-atom contributors at calculated positions, except for the disordered CH_2Cl_2 molecules. Electronic spectrum in CH_2Cl_2, λ_{max}/nm (ϵ_m/L mol^{-1} cm^{-1}): 456 (6380), 486 (5000), 540 (2720), 584 1930.

(10) Lee, S. L.; Holm, R. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 840 and references therein.

(11) (a) Roth, A.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1986**, *108*, 6823. (b) Carofiglio, T.; Floriani, C.; Roth, A.; Sgamellotti, A.; Rosi, M.; Chiesi-Villa, A.; Rizzoli, C. *J. Organomet. Chem.* **1995**, *488*, 141.

(12) Gindelberger, D. E. *Acta Crystallogr. Sect. C.* **1996**, *52*, 2493.

(13) Dolbecq, A.; Boubekeur, K.; Batail, P.; Canadell, E.; Auban-Senzier, P.; Coulon, C.; Lerstrup, K.; Bechgaard, K. *J. Mater. Chem.* **1995**, *5*, 1707.

(14) Goldberg, D. P.; Caneschi, A.; Lippard, S. J. *J. Am. Chem. Soc.* **1993**, *115*, 9299.

S0002-7863(97)03996-6 CCC: \$15.00

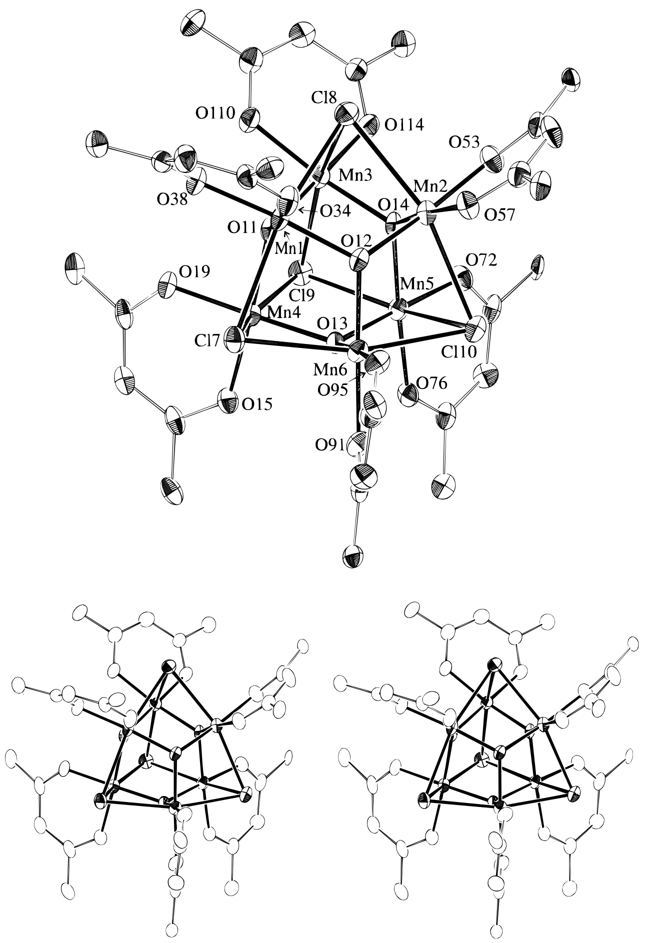

Figure 1. Labeled ORTEP plot and stereopair of $[Mn_6O_4Cl_4(Me_2dbm)_6]$ (**3**). For clarity, only the *ipso*-carbon atom of each C_6H_4-*p*-Me ring is shown. Selected distances (Å): Mn1−Mn2, 3.195(2); Mn1−Mn3, 3.207(2); Mn1−Mn4, 3.203(2); Mn1−Mn6, 3.193(2); Mn2−Mn3, 3.199(2); Mn2−Mn5, 3.210(2); Mn2−Mn6, 3.219(2); Mn3−Mn4, 3.204(2); Mn3−Mn5, 3.189(2); Mn4−Mn5, 3.205(2); Mn4−Mn6, 3.199(2); Mn5−Mn6, 3.221; Mn1−Mn5, 4.526(2); Mn2−Mn4, 4.534(2); Mn3−Mn6, 4.532(2).

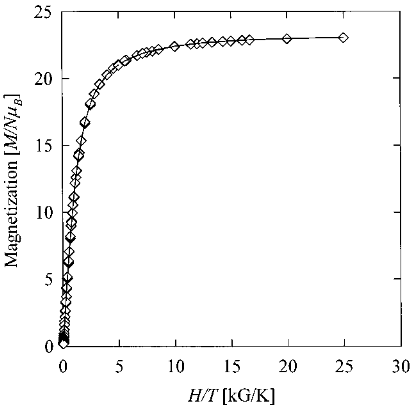

Figure 2. Plot of reduced magnetization ($M/N\mu_B$) vs H/T for $[Mn_6O_4Cl_4(Me_2dbm)_6]\cdot 0.4CH_2Cl_2$, collected in the 2.00−15.0 K and 0.50−50 kG ranges. The solid line is a fit of the data to the Brillouin function for a $S = 12$ complex with $g = 1.936$.

Variable-temperature, magnetic susceptibility data were collected on powdered $\mathbf{3}\cdot 0.4CH_2Cl_2$ in the range of 2.00−320 K. The μ_{eff}/μ_B ($\chi_m T$/cm^3 K mol^{-1}) values slowly increase from 16.01 (32.04) at 320 K to a maximum of 24.27 (73.63) at 30.0 K and then decrease to 13.69 (23.43) at 2.00 K. The maxima may be compared with 24.99 (78.0) for a $S = 12$ system with $g = 2.00$. This ground-state value was confirmed by fitting of reduced magnetization ($M/N\mu_B$) vs H/T data collected in the 0.500−50.0 kG range and temperatures down to 2.00 K (Figure 2). The $M/N\mu_B$ value saturates at 23.02, near to the value of 24 expected for $S = 12$ if $g = 2.0$. The various isofield lines are virtually superimposed, indicating essentially no zero field splitting (ZFS) within the ground state. The data were fit (solid line in Figure 2) to a Brillouin function for an isolated $S = 12$ state with $g = 1.936$ and $D = 0.0$ cm^{-1}, confirming a high-spin ground state with little or no magnetic anisotropy, as anticipated from the virtual T_d symmetry. To obtain the pairwise exchange parameters, the μ_{eff} versus T data were fit to the expression derived for a $(Mn^{III})_6$ octahedron using the Kambe vector coupling method,[15] the van Vleck equation, and exchange parameters J_{cis} and J_{trans}. The spin Hamiltonian is given in eq 1

$$\hat{H} = -2J_{cis}(\hat{S}_1\hat{S}_2 + \hat{S}_1\hat{S}_3 + \hat{S}_1\hat{S}_4 + \hat{S}_1\hat{S}_6 + \hat{S}_2\hat{S}_3 + \hat{S}_2\hat{S}_5 + \hat{S}_2\hat{S}_6 + \hat{S}_3\hat{S}_4 + \hat{S}_3\hat{S}_5 + \hat{S}_4\hat{S}_5 + \hat{S}_4\hat{S}_6 + \hat{S}_5\hat{S}_6) - 2J_{trans}(\hat{S}_1\hat{S}_5 + \hat{S}_2\hat{S}_4 + \hat{S}_3\hat{S}_6) \quad (1)$$

(where S_i is the spin of metal Mn_i), which can be transformed into the equivalent form in eq 2 by the substitutions $\hat{S}_A = \hat{S}_1 + \hat{S}_5$, $\hat{S}_B = \hat{S}_2 + \hat{S}_4$, $\hat{S}_C = \hat{S}_3 + \hat{S}_6$, and $\hat{S}_T = \hat{S}_A + \hat{S}_B + S_C$, where $\hat{S}_T$ is the resultant spin of the complete molecule. The energies,

$$\hat{H} = -J_{cis}(\hat{S}_T^{\,2} - \hat{S}_A^{\,2} - \hat{S}_B^{\,2} - \hat{S}_C^{\,2}) - J_{trans}(\hat{S}_A^{\,2} + \hat{S}_B^{\,2} + \hat{S}_C^{\,2} - \hat{S}_1^{\,2} - \hat{S}_2^{\,2} - \hat{S}_3^{\,2} - \hat{S}_4^{\,2} - \hat{S}_5^{\,2} - \hat{S}_6^{\,2}) \quad (2)$$

$E(S_T)$, of each S_T are given by eq 3, where constant terms have been omitted. An excellent fit was obtained with $J_{cis} = +8.6$ cm^{-1}, $J_{trans} = 0$ cm^{-1}, and $g = 1.965$ with TIP held constant at 1200×10^{-6} cm^3 K mol^{-1}. These J values indicate a well-isolated $S = 12$ ground state separated by 138 cm^{-1} from the first excited state.

$$E(S_T) = -J_{cis}[S_T(S_T + 1) - S_A(S_A + 1) - S_B(S_B + 1) - S_C(S_C + 1)] - J_{trans}[S_A(S_A + 1) + S_B(S_B + 1) + S_C(S_C + 1)] \quad (3)$$

The above results establish **3** as a new member of the family of high-spin molecules and represent the first time that a discrete $(Mn^{III})_6$ octahedron has been prepared. We believe it to be a prototype of a large new family of related complexes, and attempts to prepare the Br^- and other analogues are currently in progress.

Acknowledgment. This work was funded by National Science Foundation grants to G.C. and D.N.H.

Supporting Information Available: Crystallographic data collection and refinement details and listings of atomic coordinates and thermal parameters for $\mathbf{3}\cdot 3CH_2Cl_2$ (21 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA973996V

---

[15] (a) Kambe, K. *J. Phys. Soc. Jpn.* **1950**, *5*, 48. (b) Cornia, A.; Gatteschi, D.; Hegetschweiler, K. *Inorg. Chem.* **1994**, *33*, 1559.