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# High-Spin Molecules: Hexanuclear [Mn<sub>6</sub>O<sub>4</sub>Cl<sub>4</sub>(Me<sub>2</sub>dbm)<sub>6</sub>] (Me<sub>2</sub>dbmH = 4,4'- Dimethyldibenzoylmethane) with a Near Tetrahedral [Mn<sub>6</sub>O<sub>4</sub>Cl<sub>4</sub>]<sup>6+</sup> Core and a S = 12 Ground State

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**High-Spin Molecules: Hexanuclear  
[Mn<sub>6</sub>O<sub>4</sub>Cl<sub>4</sub>(Me<sub>2</sub>dbm)<sub>6</sub>] (Me<sub>2</sub>dbmH =  
4,4'-Dimethyldibenzoylmethane) with a Near  
Tetrahedral [Mn<sub>6</sub>O<sub>4</sub>Cl<sub>4</sub>]<sup>6+</sup> Core and a S = 12  
Ground State**

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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* ≈ 16½ for one of the clusters in a sample of cocrystallized Fe<sub>17</sub> and Fe<sub>19</sub> species,<sup>2</sup> but examples with *S* ≥ 8 are nevertheless very rare.<sup>3,4</sup> 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<sub>x</sub>* 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<sub>B</sub>*).<sup>3a,5,6</sup> 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<sup>III</sup> cluster with an aesthetically pleasing [Mn<sub>6</sub>O<sub>4</sub>-

Cl<sub>4</sub>]<sup>6+</sup> core and show that it possesses a *S* = 12 ground state, one of the highest yet identified.

Treatment of [Mn<sub>4</sub>O<sub>2</sub>(O<sub>2</sub>CMe)<sub>6</sub>(py)<sub>2</sub>(Me<sub>2</sub>dbm)<sub>2</sub>] (**1**) (Me<sub>2</sub>dbmH = 4,4'-dimethyldibenzoylmethane), prepared as for the dbm analogue,<sup>7</sup> in CH<sub>2</sub>Cl<sub>2</sub> with 6 equiv of Me<sub>3</sub>SiCl and 2 equiv of Me<sub>2</sub>dbmH gave a brown solution from which was isolated crude [MnCl(Me<sub>2</sub>dbm)<sub>2</sub>] (**2**) on addition of Et<sub>2</sub>O. Redissolution in MeCN:CH<sub>2</sub>Cl<sub>2</sub> (1:1) followed by standing and slight concentration at room temperature over ~3 weeks gave black crystals of [Mn<sub>6</sub>O<sub>4</sub>Cl<sub>4</sub>(Me<sub>2</sub>dbm)<sub>6</sub>]·3CH<sub>2</sub>Cl<sub>2</sub> (3·3CH<sub>2</sub>Cl<sub>2</sub>), 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<sub>2</sub>Cl<sub>2</sub> (1:1), and subsequent treatment as above, suggesting the formation of **3** to involve a slow hydrolysis of the mononuclear species.<sup>8</sup> Nonoptimized yields up to 14% have been obtained to date.<sup>8</sup>

The structure<sup>9</sup> of **3** (Figure 1) consists of a (Mn<sup>III</sup>)<sub>6</sub> octahedron with four nonadjacent faces bridged by the μ<sub>3</sub>-O<sup>2-</sup> ions and the other four faces by μ<sub>3</sub>-Cl<sup>-</sup> ions. Six-coordinate, approximately octahedral geometry at each metal is completed by a chelating Me<sub>2</sub>dbm group. The cluster has virtual *T<sub>d</sub>* symmetry. As expected for high-spin, octahedral Mn<sup>III</sup>, 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<sup>2-</sup> (1.876(4)–1.899(5) Å) and Mn–O(Me<sub>2</sub>dbm) (1.903(5)–1.925(5) Å) bond lengths are as expected. As a result of (i) the long Mn–Cl<sup>-</sup> versus short Mn–O<sup>2-</sup> 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<sub>6</sub>O<sub>4</sub>Cl<sub>4</sub>]<sup>6+</sup> core is a near tetrahedron with a Cl<sup>-</sup> at each vertex, a Mn at the midpoint of each edge, and a O<sup>2-</sup> bridging each face. Although many [M<sub>6</sub>(μ<sub>3</sub>-X)<sub>8</sub>] face-capped metal octahedra are known,<sup>10</sup> only a relative few contain two types of X group, e.g., the [Ti<sub>6</sub>O<sub>6</sub>Cl<sub>2</sub>],<sup>11</sup> [Ti<sub>6</sub>Te<sub>6</sub>O<sub>2</sub>],<sup>12</sup> and [Re<sub>6</sub>Y<sub>x</sub>Z<sub>8-x</sub>] (*x* = 5, Y = S or Se, Z = Cl; *x* = 6, Y = S, Z = Cl)<sup>13</sup> cores. Only the [Ti<sub>6</sub>(μ<sub>3</sub>-O)<sub>4</sub>(μ<sub>3</sub>-Cl)<sub>4</sub>] core of [(C<sub>5</sub>H<sub>5</sub>Me)<sub>6</sub>Ti<sub>6</sub>O<sub>4</sub>Cl<sub>4</sub>]<sup>11</sup> contains, like **3**, four O<sup>2-</sup> and 4 Cl<sup>-</sup> bridges, but the structure does not approximate to a tetrahedron. [Mn<sup>III</sup><sub>6</sub>X<sub>8</sub>] species have been unknown to date, although a [Mn<sub>6</sub>(μ<sub>3</sub>-O)<sub>4</sub>(μ<sub>3</sub>-Cl)<sub>4</sub>]<sup>4+</sup> unit as found in **3** but at the 2Mn<sup>II</sup>, 4Mn<sup>III</sup> level is also a recognizable fragment within the higher nuclearity cluster [Mn<sub>10</sub>O<sub>4</sub>Cl<sub>12</sub>(biphen)<sub>4</sub>]<sup>4-</sup> (biphen = 2,2'-biphenoxide).<sup>14</sup>

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(8) The reaction is more complicated than this statement suggests, with [Mn(Me<sub>2</sub>dbm)<sub>3</sub>] 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<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub>. <sup>1</sup>H NMR spectra in these solvents suggest the structure is retained on dissolution.

(9) Dried solid analyzed as 3·0.4CH<sub>2</sub>Cl<sub>2</sub>. Anal. Calcd (found) for C<sub>102.4</sub>H<sub>90.8</sub>O<sub>16</sub>Cl<sub>4.8</sub>Mn<sub>6</sub>: C, 59.21 (59.28); H, 4.49 (4.41). Crystal data for 3·3CH<sub>2</sub>Cl<sub>2</sub>: monoclinic; *P*2<sub>1</sub>/c; *a* = 17.172(2) Å, *b* = 18.302(2) Å, *c* = 34.534(4) Å; β = 100.36(1)°; *Z* = 4; *V* = 10677 Å<sup>3</sup>; *d*<sub>calcd</sub> = 1.430 g cm<sup>-3</sup>; *T* = -171 °C. The structure was solved using MULTAN and refined on *F* to *R*(*R<sub>w</sub>*) = 5.80 (5.73) using 9989 unique reflections with *F* > 2.33σ(*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<sub>2</sub>-Cl<sub>2</sub> molecules. Electronic spectrum in CH<sub>2</sub>Cl<sub>2</sub>, λ<sub>max</sub>/nm (ε<sub>m</sub>/L mol<sup>-1</sup> cm<sup>-1</sup>): 456 (6380), 486 (5000), 540 (2720), 584 1930.

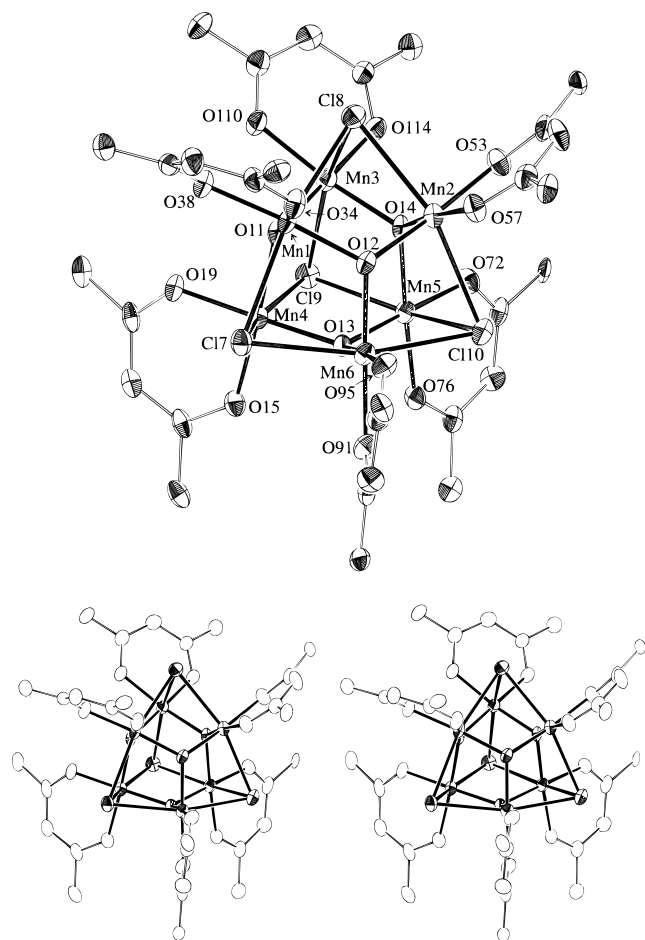
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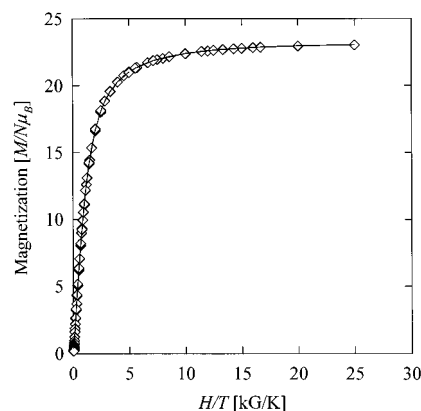
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**Figure 1.** Labeled ORTEP plot and stereopair of  $[\text{Mn}_6\text{O}_4\text{Cl}_4(\text{Me}_2\text{dbm})_6]$  (**3**). For clarity, only the *ipso*-carbon atom of each  $\text{C}_6\text{H}_4$ -*p*-Me ring is shown. Selected distances (Å): Mn1–Mn2, 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(2); Mn1–Mn5, 4.526(2); Mn2–Mn4, 4.534(2); Mn3–Mn6, 4.532(2).

Variable-temperature, magnetic susceptibility data were collected on powdered **3**· $0.4\text{CH}_2\text{Cl}_2$  in the range of 2.00–320 K. The  $\mu_{\text{eff}}/\mu_{\text{B}}$  ( $\chi_{\text{m}}T/\text{cm}^3 \text{ K mol}^{-1}$ ) 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 ( $M/N\mu_{\text{B}}$ ) vs  $H/T$  data collected in the 0.500–50.0 kG range and temperatures down to 2.00 K (Figure 2). The  $M/N\mu_{\text{B}}$  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  $D = 0.0 \text{ cm}^{-1}$ , confirming a high-spin ground state with little or no magnetic anisotropy, as anticipated from the



**Figure 2.** Plot of reduced magnetization ( $M/N\mu_{\text{B}}$ ) vs  $H/T$  for  $[\text{Mn}_6\text{O}_4\text{Cl}_4(\text{Me}_2\text{dbm})_6] \cdot 0.4\text{CH}_2\text{Cl}_2$ , 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  $g = 1.936$ .

virtual  $T_d$  symmetry. To obtain the pairwise exchange parameters, the  $\mu_{\text{eff}}$  versus  $T$  data were fit to the expression derived for a  $(\text{Mn}^{\text{III}})_6$  octahedron using the Kambe vector coupling method,<sup>15</sup> the van Vleck equation, and exchange parameters  $J_{\text{cis}}$  and  $J_{\text{trans}}$ . The spin Hamiltonian is given in eq 1

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

(where  $S_i$  is the spin of metal  $\text{Mn}_i$ ), which can be transformed into the equivalent form in eq 2 by the substitutions  $\hat{S}_{\text{A}} = \hat{S}_1 + \hat{S}_5$ ,  $\hat{S}_{\text{B}} = \hat{S}_2 + \hat{S}_4$ ,  $\hat{S}_{\text{C}} = \hat{S}_3 + \hat{S}_6$ , and  $\hat{S}_{\text{T}} = \hat{S}_{\text{A}} + \hat{S}_{\text{B}} + \hat{S}_{\text{C}}$ , where  $\hat{S}_{\text{T}}$  is the resultant spin of the complete molecule. The energies,

$$\hat{H} = -J_{\text{cis}}(\hat{S}_{\text{T}}^2 - \hat{S}_{\text{A}}^2 - \hat{S}_{\text{B}}^2 - \hat{S}_{\text{C}}^2) - J_{\text{trans}}(\hat{S}_{\text{A}}^2 + \hat{S}_{\text{B}}^2 + \hat{S}_{\text{C}}^2 - \hat{S}_1^2 - \hat{S}_2^2 - \hat{S}_3^2 - \hat{S}_4^2 - \hat{S}_5^2 - \hat{S}_6^2) \quad (2)$$

$E(S_{\text{T}})$ , of each  $S_{\text{T}}$  are given by eq 3, where constant terms have been omitted. An excellent fit was obtained with  $J_{\text{cis}} = +8.6$

$$E(S_{\text{T}}) = -J_{\text{cis}}[S_{\text{T}}(S_{\text{T}} + 1) - S_{\text{A}}(S_{\text{A}} + 1) - S_{\text{B}}(S_{\text{B}} + 1) - S_{\text{C}}(S_{\text{C}} + 1)] - J_{\text{trans}}[S_{\text{A}}(S_{\text{A}} + 1) + S_{\text{B}}(S_{\text{B}} + 1) + S_{\text{C}}(S_{\text{C}} + 1)] \quad (3)$$

$\text{cm}^{-1}$ ,  $J_{\text{trans}} = 0 \text{ cm}^{-1}$ , and  $g = 1.965$  with TIP held constant at  $1200 \times 10^{-6} \text{ cm}^3 \text{ K mol}^{-1}$ . These  $J$  values indicate a well-isolated  $S = 12$  ground state separated by  $138 \text{ cm}^{-1}$  from the first excited state.

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

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**Supporting Information Available:** Crystallographic data collection and refinement details and listings of atomic coordinates and thermal parameters for **3**· $3\text{CH}_2\text{Cl}_2$  (21 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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