A Ferromagnetic Ring of Six Manganese(III) Ions with a $S = 12$ Ground State

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The design of novel high-spin molecules represents a major goal of current research in the field of nanoscale materials. In particular, the synthesis of large transition-metal ion clusters has provided excellent materials for the observation of unusual physical properties, such as quantum tunneling of the magnetization and magnetic hysteresis effects of purely molecular origin.[1] Unfortunately, large molecular clusters are almost invariably obtained in a serendipitous manner from self-assembly reactions and general strategies for the synthesis of large clusters with preordained structures and properties have not yet been developed. We recently suggested that host−guest interactions are among the available tools for a fine-tuning of the structure and properties of magnetic clusters.[2a] We now show that the magnetic properties of high-nuclearity clusters may be varied to a very large extent by acting on the electronic structure of the constituent metal ions. By substituting iron(III) with manganese(III) in the core of the cyclic cluster [NaFe$_6$(OMe)$_{12}$(dbm)$_6$]$^+$ (**1**) (Hdbm = dibenzoylmethane),[2b,c] we were able to switch from a $S = 0$ to a $S = 12$ ground state. Changing the number of d electrons on the metal centers may therefore represent a powerful tool for modulating the properties of single-molecule magnets.

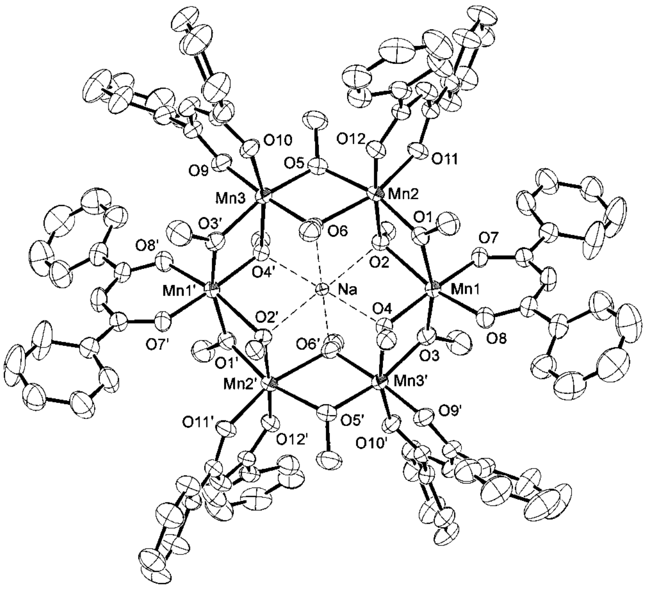

Figure 1. ORTEP drawing showing the molecular structure of **2** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

The complex [NaMn$_6$(OMe)$_{12}$(dbm)$_6$]$^+$ (**2**) was synthesized from manganese(II) dichloride by simultaneous oxidation *and* methoxide-promoted aggregation. A one-pot reaction involving MnCl$_2$ (1 equiv), dibenzoylmethane (1 equiv), NaOMe (4 equiv), and dioxygen in anhydrous methanol, followed by recrystallization from CHCl$_3$/MeOH mixtures in the presence of NaBPh$_4$, afforded black-brown crystals of [**2**]BPh$_4$.[3] A single-crystal X-ray investigation at 188 K[4] pointed to a cyclic structure with approximate S_6 point-group symmetry but crystallographic C_i symmetry (Figure 1). The [Mn$_6$(OMe)$_{12}$] ring displays a 12-metallacrown-6 structure and acts as a host for an alkali-metal ion,[2] which has a trigonally distorted octahedral environment. Although the average nearest-neighbor Mn···Mn distance [3.21(2) Å] compares well with that observed in **1** [3.194(9) Å], the coordination environment of the metal ions shows important differences.[5] A tetragonal elongation of the coordination polyhedra is evident along the O8−Mn1−O2, O11−Mn2−O6, and O10−Mn3−O4′ directions, which are roughly perpendicular to each other as a consequence of edge-sharing between MnO$_6$ octahedra (Figure 2). Axial bonds involve oxygen atoms from dbm and μ_3-OMe ligands and have unequal lengths [average: 2.06(2) and 2.23(4) Å, respectively]. Two trans equatorial sites are occupied by μ_2-OMe ligands [average Mn−O: 2.00(3) Å]. The remaining oxygen of dbm and a μ_3-OMe ligand (involved in an axial bond with an adjacent metal ion) act as in-plane donors with much shorter Mn−O distances [average: 1.910(8) Å]. The observed coordination geometry of the metal

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(1) (a) Thomas, L.; Lionti, F.; Ballou, R.; Gatteschi, D.; Sessoli, R.; Barbara, B. *Nature* **1996**, *383*, 145. (b) 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. (c) Sessoli, R. Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141. (d) Barra, A.-L.; Caneschi, A.; Gatteschi, D.; Sessoli, R. *J. Am. Chem. Soc.* **1995**, *117*, 8855.

(2) (a) Abbati, G. L.; Cornia, A.; Fabretti, A. C.; Malavasi, W.; Schenetti, L.; Caneschi, A.; Gatteschi, D. *Inorg. Chem.* **1997**, *36*, 6443. (b) Caneschi, A.; Cornia, A.; Fabretti, A. C.; Foner, S.; Gatteschi, D.; Grandi, R.; Schenetti, L. *Chem.—Eur. J.* **1996**, *2*, 1379. (c) Caneschi, A.; Cornia, A.; Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 467.

(3) Anal. Calcd for [**2**]BPh$_4$·1.2CHCl$_3$: C, 60.46; H, 4.91; Cl, 5.05; Mn, 13.04. Found (vacuum-treated sample: 1 h, 0.2 mmHg): C, 60.52; H, 5.17; Cl, 4.78; Mn, 12.38. UV−vis (solid): 10 000 (D_4: $^5A_1 \leftarrow {}^5B_1$), 18 000 (D_4: $^5B_2 \leftarrow {}^5B_1$), 21 000 cm^{-1} (D_4: $^5E \leftarrow {}^5B_1$).

(4) Crystal data for [**2**]BPh$_4$·xCHCl$_3$ ($x = 2$): Mn$_6$NaO$_{24}$C$_{128}$H$_{124}$Cl$_6$B, fw = 2622.41, $T = 188(2)$ K; triclinic, space group $P\bar{1}$ (No. 2), $a = 14.392(3)$ Å, $b = 16.790(2)$ Å, $c = 17.344(3)$ Å, $\alpha = 61.42(1)°$, $\beta = 72.36(1)°$, $\gamma = 88.96(2)°$, $V = 3466.8(10)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.256$ g cm^{-3}, $\rho_{obsd} = 1.44(1)$ g cm^{-3}, $\lambda = 0.710\,69$ Å, $\mu = 0.71$ mm^{-1}. For 14 516 unique reflections and 944 parameters, w$R2 = 0.2741$ and $R1 = 0.0783$ [on 9862 observed reflections with $I > 2\sigma(I)$].[10] The BPh$_4$ anion was found in general positions and refined with half-occupancy. Two highly disordered chloroform molecules per unit cell were located. Residual peaks (≤ 0.9 e Å^{-3}) probably arising from additional, highly disordered CHCl$_3$ and/or MeOH molecules (see ρ_{calcd} vs ρ_{obsd}) were not assigned.

(5) Selected bond lengths (Å): Mn1−O1, 1.988(3); Mn1−O2, 2.274(3); Mn1−O3, 1.973(3); Mn1−O4, 1.921(3); Mn1−O7, 1.904(3); Mn1−O8, 2.074(3); Mn2−O1, 2.006(3); Mn2−O2, 1.903(3); Mn2−O5, 2.052(3); Mn2−O6, 2.196(3); Mn2−O11, 2.042(3); Mn2−O12, 1.901(3); Mn3−O3′, 2.013(3); Mn3−O4′, 2.215(3); Mn3−O5, 1.963(3); Mn3−O6, 1.914(3); Mn3−O9, 1.914(3); Mn3−O10, 2.070(3); Na−O2, 2.306(3); Na−O4, 2.305(3); Na−O6, 2.291(3). Interbond angles (deg): Mn1−O1−Mn2, 107.72(15); Mn2−O2−Mn1, 100.74(14); Mn1−O3−Mn3′, 106.7(2); Mn1−O4−Mn3′, 101.02(13); Mn3−O5−Mn2, 105.7(2); Mn3−O6−Mn2, 102.1(2). Nonbonded distances (Å) and angles (deg): Mn1−Mn2, 3.2258(10); Mn2−Mn3, 3.2011(11); Mn1−Mn3′, 3.1972(10); Mn3−Mn2−Mn1, 119.85(3); Mn1′−Mn3−Mn2, 119.55(3); Mn3′−Mn1−Mn2 119.92(3).

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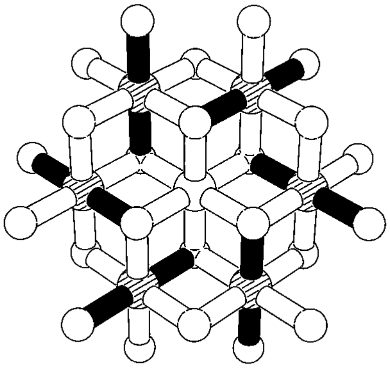

Figure 2. Sketched structure of the Mn/O/Na core of **2** in the context of an idealized CdI_2 lattice. The peculiar "whirlpool" arrangement of elongation axes (black) is highlighted.

ions and the UV−vis spectra in the solid state[3] are both typical of Jahn−Teller-distorted high-spin manganese(III).[6] This strongly suggests the presence of six manganese(III) ions in the cluster and is consistent with charge-balance requirements.

The χT vs T curve for a microcrystalline sample of [**2**]BPh_4 clearly reveals a tendency of the Mn^{III} spins to align in a parallel fashion at low temperature (Figure 3).[7] The χT value at 260 K (26.0 emu·K·mol^{-1}) is larger than expected for six uncoupled $S = 2$ spins (18.0 emu·K·mol^{-1} with $g = 2.00$). With decreasing temperature, the χT product increases, reaching 71.0 emu·K·mol^{-1} at 5 K. This value is close to the limit of 78.0 emu·K·mol^{-1} expected for parallel alignment of the spins to give a ground $S = 12$ state. Comparison of the χT values measured at low temperature with those expected for the various ground configurations proves that the six coupling constants are ferromagnetic, although not necessarily equal to each other. Attempts were made to fit the data on the assumption of identical coupling constants in the ring, but this does not account for the observed magnetic behavior, as shown in Figure 3 (dashed line). Since from the structural point of view it would be possible to choose up to three different j constants, we first attempted to use two constants. By setting $j_{12} = j_{23} = j_{45} = j_{56} = j_A$ and $j_{34} = j_{61} = j_B$, we could accurately reproduce the experimental data down to 15 K with $j_A = -23.8$ cm^{-1}, $j_B = -2.6$ cm^{-1}, and $g = 2.00$ (solid line in Figure 3). At first sight, a 1-order-of-magnitude difference between j_A and j_B is surprising, though it is consistent with the significant departures from 6-fold symmetry observed in the structure. While the Mn2···Mn3 and Mn3···Mn1′ separations are equal within experimental error [3.2011(11) and 3.1972(10) Å, respectively], Mn1···Mn2 is significantly longer [3.2258(10) Å]. Furthermore, axial distortion is more pronounced for Mn1 [Mn1−O2, 2.274(3) Å] than for the remaining metal ions [Mn2−O6 = 2.196(3) Å; Mn3−O4′ = 2.215(3) Å]. The ferromagnetic nature of exchange-coupling interactions in **2** can be explained by assuming prevalent e_g−e_g contributions. Given the elongated nature of the distortion from octahedral symmetry, the metal $x^2 - y^2$ orbitals are empty. Due to the arrangement of local elongation axes in the structure, the z^2 magnetic orbitals have a nonzero overlap with the empty $x^2 - y^2$ orbitals through μ_3-OMe ligands. This $x^2 - y^2/z^2$ pathway is expected to provide a ferromagnetic contribution to magnetic coupling.[8]

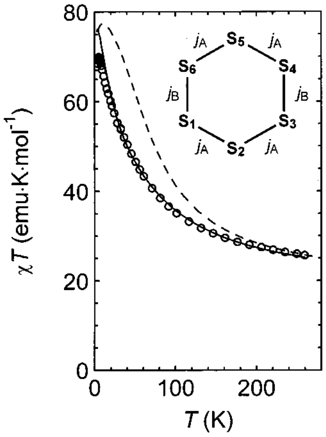

Figure 3. Experimental χT vs T curve measured on a microcrystalline sample of [**2**]BPh_4. The calculated curves for $j_A = -23.8$ cm^{-1}, $j_B = -2.6$ cm^{-1}, $g = 2.00$ (solid line) and $j_A = j_B = -16.6$ cm^{-1} (dashed line) are also shown.

The low-temperature magnetism of [**2**]BPh_4 was further investigated by magnetization vs field measurements.[7] On the assumption of an isolated $S = 12$ multiplet with axial zero-field splitting, the experimental data could be fitted with $g = 1.80$ and $D = -0.12$ cm^{-1}. The best-fit g value is unusually low for a Mn^{III} complex[6] and may reflect the presence of low-lying multiplets with $S < 12$.

In conclusion, a novel high-nuclearity transition-metal cluster with 24 unpaired electrons in the ground state has been synthesized. Its cyclic structure is unprecedented among high-nuclearity ($n \geq 6$) manganese(III) complexes.[9] Comparison with previous work on iron(III)−alkoxide clusters reveals an outstanding tendency of oxygen atoms of OMe and dbm ligands to assemble into two closest-packing layers under the adopted experimental conditions (Figure 2).[2] We suggest that full exploitation of this tendency for addressing the synthesis of molecular clusters with a planar arrangement of metal ions may represent a possible starting point for designing the structure and properties of large magnetic clusters.

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Supporting Information Available: Text giving full experimental details for the synthesis of [**2**]BPh_4 and listings and graphical representations of molar magnetic susceptibility vs temperature and magnetization vs field data (5 pages). An X-ray crystallographic file, in CIF format, for [**2**]BPh_4 is available on the Internet only. Ordering and access information is given on any current masthead page.

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(6) Barra, A. L.; Gatteschi, D.; Sessoli, R.; Abbati, G. L.; Cornia, A.; Fabretti, A. C.; Uytterhoeven, M. G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2329.

(7) Microcrystalline samples were subject to prolonged pumping before experiment. Magnetic fields of 10 kG for $30 \leqslant T \leqslant 260$ K and 1 kG for $2.3 \leqslant T < 30$ K were used in magnetic susceptibility vs T runs on a Parafilm-restrained sample. Magnetization experiments were performed at 2.0 and 4.0 K in the field range 0−70 kG on a Vaseline-restrained sample.

(8) Ginsberg, A. *Inorg. Chim. Acta Rev.* **1971**, *5*, 45.

(9) Mn_7: (a) Wang, S.; Tsai, H.-L.; Streib, W. E.; Christou, G.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1992**, 677. Mn_8 and Mn_9: (b) Tsai, H.-L.; Wang, S.; Folting, K.; Streib, W. E.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1995**, *117*, 2503. (c) Grillo, V. A.; Knapp, M. J.; Bollinger, J. C.; Hendrickson, D. N.; Christou, G. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1818. Mn_{18}: (d) Squire, R. C.; Aubin, S. M. J.; Folting, K.; Streib, W. E.; Christou, G.; Hendrickson, D. N. *Inorg. Chem.* **1995**, *34*, 6463.

(10) Sheldrick, G. M. SHELXL-93: Program for Crystal Structure Refinement. Universität Göttingen, 1993.