# Variation in the Electron Count and Ground State of [Mn$_{12}$O$_{12}$(O$_2$CR)$_{16}$(H$_2$O)$_4$] (R = Me or Ph) by Metal Substitution and Redox Changes: Preparation and Properties of [Mn$_8$Fe$_4$O$_{12}$(O$_2$CMe)$_{16}$(H$_2$O)$_4$]·4H$_2$O·2MeCO$_2$H and [NPr$^n_4$] [Mn$_{12}$O$_{12}$(O$_2$CPh)$_{16}$(H$_2$O)$_4$]·H$_2$O

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As a means of varying the electron count of complexes [Mn$_{12}$O$_{12}$(O$_2$CR)$_{16}$(H$_2$O)$_4$] (1; R = Me or Ph), the aggregates [Mn$_8$Fe$_4$O$_{12}$(O$_2$CMe)$_{16}$(H$_2$O)$_4$] 2 and [NPr$^n_4$] [Mn$_{12}$O$_{12}$(O$_2$CPh)$_{16}$(H$_2$O)$_4$] 3 have been prepared; magnetochemical measurements confirm that the unusual properties of 1 can be significantly altered by 'conversion' to 2 and 3.

An important current area of research is the development of synthetic methodologies for molecular species possessing large spin ground states, and their employment as building blocks to prepare new molecular ferromagnets.[1–3] A number of such molecular ferromagnets are currently known that consist of organic[2] or inorganic[3] molecular units. The challenge is to access suitable molecules and spatially arrange them in an appropriate manner; also important would be the ability to alter in a controllable manner the spin of the building-block molecule without changing its structure and thus permit access to a family of related materials with differing properties suitable for perhaps different applications. We recently reported that magnetization measurements (10.0, 30.0 and 48.0 kG) and magnetic susceptibility (10.0 kG; 5–300.8 K) data indicate an $S = 14$ ground spin state for [Mn$_{12}$O$_{12}$(O$_2$CPh)$_{16}$(H$_2$O)$_4$] 1a;[4] Alternating current susceptometry data at near to zero field indicate an $S = 10$ ground state for [Mn$_{12}$O$_{12}$(O$_2$CMe)$_{16}$(H$_2$O)$_4$] 1b.[5] Given the potential of such aggregates as building blocks to molecular ferromagnets, we have sought to vary their ground states by altering their electron count (8Mn$^{III}$, 4Mn$^{IV}$; 44 d electrons) and herein report the successful attainment of this objective *via* two means: partial Fe$^{III}$ (d$^5$)-for-Mn$^{III}$ (d$^4$) substitution, and one-electron reduction.

To a stirred slurry of Fe(O$_2$CMe)$_2$ in 60% (v/v) MeCO$_2$H–H$_2$O were slowly added 0.39 equiv. of KMnO$_4$, followed by

slow heating to 60 °C. The cooled solution was layered with acetone and, after several days, black crystals of [Mn$_8$Fe$_4$O$_{12}$(O$_2$CMe)$_{16}$(H$_2$O)$_4$] 2 as the 4H$_2$O·2MeCO$_2$H solvate were obtained in 85% yield based on Mn.† Crystals of 2·4H$_2$O·2MeCO$_2$H are isomorphous with 1b·4H$_2$O·2Me-CO$_2$H,[6] and the structure‡ (Fig. 1) confirms retention of the [M$_{12}$O$_{12}$]$^{16+}$ core. Interestingly, the Fe$^{III}$ locations are

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**Fig. 1** The structure of complex **2**. The peripheral ligands are de-emphasized for clarity and depicted as spheres of arbitrary size. Selected distances (Å): Mn(1)···Mn(1'), 2.820(4); Mn(1)···Mn(1'''), 2.938(4); Mn(1)···Mn(2), 2.773(3); Mn(1)···Fe(3), 3.478(3); Mn(1)···Fe(3''), 3.465(3); Mn(2)···Fe(3), 3.357(3); Mn(2)···Fe(3''), 3.446(3); Mn(1)–O(1), 1.883(10); Mn(1)–(O'), 1.924(9); Mn(1)–O(1''), 1.936(9); Mn(1)–O(2), 1.878(9); Mn(1)–O(3), 1.852(9); Mn(1)–O(4), 1.934(9); Mn(2)–O(2), 1.890(9); Mn(2)–O(3), 1.887(9); Mn(2)–O(5), 2.226(10); Mn(2)–O(6), 2.231(11); Mn(2)–O(8), 1.953(10), Mn(2)–O(10), 1.953(11); Fe(3)–O(2), 1.937(9); Fe(3)–O(3'), 1.925(9); Fe(3)–O(7), 2.037(10), Fe(3)–O(9), 2.025(10); Fe(3)–O(11), 2.035(10); Fe(3)–O(12), 2.097(10).

ordered, and are identifiable from metric parameters and the absence of Jahn–Teller distortions clearly present in **1a** and **1b**. Thus, Fe(3)–O bonds are in the narrow range 1.925(9)–2.097(10) Å [cf. 1.892(7)–2.178(9) Å at these sites in **1b**] whereas the Mn(2)–O bonds of **2** are in the range 1.887(9)–2.231(11) Å. Elemental analysis of products from multiple preparations indicate the actual Mn:Fe ratio to be ca. 7.64:4.36, suggesting some partial occupation of the Mn(2) sites by Fe$^{III}$.§ This additional Fe was observed in the Mössbauer spectrum at 300 K as a weak doublet [δ 0.405(10), ΔE$_Q$ 1.061(2) mm s$^{-1}$] flanking the intense doublet [δ 0.416(2), ΔE$_Q$ 0.459(4) mm s$^{-1}$] of Fe(3).

The cyclic voltammogram (CV) of **1a** in CH$_2$Cl$_2$ displays quasi-reversible oxidations and reductions at 0.79 and 0.06 V, respectively, vs. ferrocene. Treatment of **1a** in CH$_2$Cl$_2$ with 1 equivalent of NPr$^n_4$I followed by addition of EtO$_2$CMe–Et$_2$O (2:1) gave a precipitate of [NPr$^n_4$][Mn$_{12}$O$_{12}$(O$_2$CPh)$_{16}$-(H$_2$O)$_4$]·H$_2$O **3** in 74% yield. The PPh$_4^+$ salt was prepared similarly using PPh$_4$I. Elemental analyses¶ and IR and NMR spectra are in agreement with the indicated formulation, and conductivity determinations in MeCN gave values of 97 and 107 ohm$^{-1}$ mol$^{-1}$ cm$^2$ for the Pr$^n_4$N$^+$ and PPh$_4^+$ salts,

§ Multiple analyses (of different preparations) have yielded ranges for the metal content of Mn, 7.50–7.77 and Fe, 4.23–4.50. These are satisfyingly narrow ranges given the experimental errors inherent in metal analyses.

¶ The analytical data for **3** (C, H, N, Mn) and the PPh$_4^+$ derivative (C, H, Mn) were satisfactory.

respectively, consistent with 1:1 electrolytes. The CV of **3** displayed two oxidations at the same potentials as for **1a**. We are confident that the anion of **3** is the reduced version of **1a** with no (major) structural change.

Variable-temperature magnetic susceptibility data have been recorded at 10.0 kG for powdered samples of complexes **2** and **3**. For **2**·4H$_2$O·2MeCO$_2$H, the effective magnetic moment (μ$_{eff}$) per molecule steadily decreases from 10.66 μ$_B$ at 300 K to 5.29 μ$_B$ at 9.01 K, whereupon it begins to decrease more rapidly to 4.06 μ$_B$ at 2.00 K (Fig. 2). This behaviour is consistent with an $S$ = 2 ground state, with the low-temperature behavior most likely due to Zeeman and zero-field splitting effects. While much additional study is required to characterize fully the electronic structure of **2**, the data obtained to date are clearly dramatically different from those for complex **1b** ($S$ = 10). For the latter, μ$_{eff}$ for a powder sample at 10.0 kG slowly increases with decreasing temperature, reaching a maximum of 20.4 μ$_B$ at ca. 10 K and then dropping rapidly at lower temperatures.[5] The increased electron count of **2** (4Mn$^{III}$, 4Fe$^{III}$, 4Mn$^{IV}$; 48 d electrons) has thus led to a striking decrease in the spin of the ground state. This may be rationalized as arising from an increased contribution from antiferromagnetic exchange interactions and this is itself consistent with an increased electron count in the metal e$_g$ orbitals; for example, in isostructural Mn$_4^{III}$ and Fe$_4^{III}$ complexes, the former are known to exhibit weaker antiferromagnetic interactions than the latter,[7] and Fe$^{III}_2$ species are almost always antiferromagnetically coupled.[8] It is likely that the topological arrangement of metal ions in **1a, 1b**,
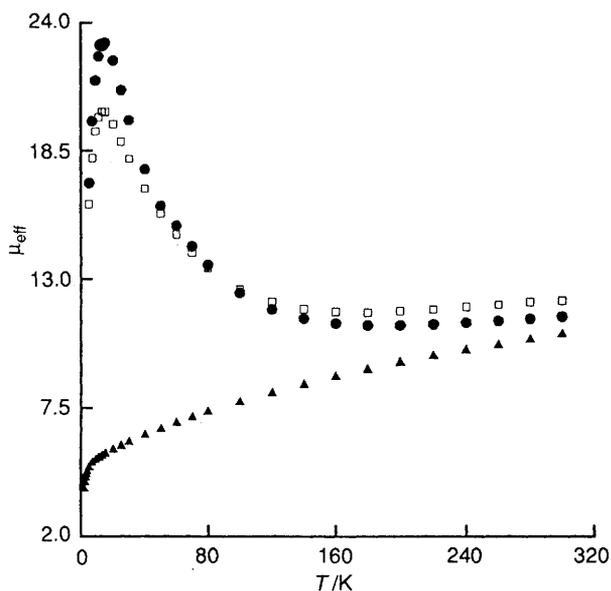
**Fig. 2** Plots of effective magnetic moment per molecule *versus* temperature for powder samples in a 10.0 kG field for: (●) complex **1a**. (▲) complex **2**·4H$_2$O·2MeCO$_2$H; (□) complex **3**

2 and 3 leads to spin frustration[9] and that this is also important in determining the spin of the ground state.

For complex **3**, $\mu_{eff}$ per molecule slowly decreases from 12.10 $\mu_B$ at 300 K to 11.60 $\mu_B$ at 180 K, then slowly increases, reaching a maximum of 20.21 $\mu_B$ at 13.0 K, and finally decreases to 16.20 $\mu_B$ at 5.01 K (Fig. 2). This behaviour is similar to that observed for **1a** ($S = 14$) except that the latter displays larger $\mu_{eff}$ values, reaching a maximum of 23.22 $\mu_B$ at 10 K.[4] Again, much detailed study will be necessary to fully characterize **3**, but it does appear to possess a lower spin ground state than **1a**. As for **2**, the proposed rationalization is that the addition of the extra electron in **3** (9Mn$^{III}$, 3Mn$^{IV}$; 45 d electrons) into an e$_g$ orbital is increasing the antiferromagnetic contribution to the exchange interactions in the molecule.

In summary, it is clear that alterations to the electron count of [Mn$_{12}$O$_{12}$(O$_2$CR)$_{16}$(H$_2$O)$_4$] are indeed possible, by both metal replacement and redox changes, and that this leads to major changes in the spin of the ground state of the species. Further detailed study of complexes **1–3** and access to other [Mn$_x$M$_{12-x}$O$_{12}$] (M = Fe$^{III}$, V$^{III}$, Cr$^{III}$, *etc.*) complexes are objectives of future work, as are the linking of these species to form one-, two- and three-dimensional extended arrays.

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