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New routes to high nuclearity cages: a fluoride-based hexaicosametallic manganese cage

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The reaction of MnF_3 with benzotriazole (BTAH) in hot MeOH gives the Mn(III) complex $[Mn_{26}O_{16}(OH)_{10}(OMe)_6(F)_{10}(BTA)_{20}(BTAH)_2(MeOH)_{13}(H_2O)]$ which displays hysteresis and temperature-independent magnetisation relaxation at low temperature.

The interest in the synthesis of high nuclearity cages of paramagnetic 3d-metals resulted from the discovery that the complex $[Mn_{12}O_{12}(O_2CH_3)_{16}(H_2O)_4]$ could function as a nanoscale magnet below a critical blocking temperature.[1] Since then a number of other compounds, containing not just Mn but Fe, Ni and V, have been reported to act as single-molecule magnets (SMMs).[2–9] In order to function as a SMM a molecule must display the combination of a relatively large spin ground state and large and negative easy-axis-type anisotropy. By far the best examples of SMMs are those compounds containing Mn. A 'problem' in this respect is the lack of a suitable source of Mn^{3+} and a reliance on oxidizing Mn^{2+}, or the use of the triangles $[Mn_3O(O_2CR)_6L_3]^{0/+}$.[10] Metal fluorides have been used to great effect in the synthesis of polymetallic chromium carboxylates[11] and more recently in the synthesis of an open-shell Keggin iron ion,[12] but have thus far never been used in manganese cluster chemistry. Herein we report the synthesis, structure and initial magnetic properties of a new hexaicosametallic manganese cage made from MnF_3 which is not only the second largest Mn cage yet reported, but highly unusual in that it contains primarily nitrogen donor ligands.

Reaction of anhydrous MnF_3 with three equivalents of benzotriazole (BTAH), under an inert atmosphere at 100 °C, followed by extraction in hot MeOH gives a black solution from which crystals of $[Mn_{26}O_{16}(OH)_{10}(OMe)_6(F)_{10}(BTA)_{20}(BTAH)_2(MeOH)_{13}(H_2O)]$. MeOH **1** are obtained upon diffusion of Et_2O after two weeks. The yield is low (< 5%) but reproducible. The structure†‡ reveals a complex molecule (Fig. 1) whose $[Mn^{III}_{26}O_{16}(OH)_{10}(OMe)_6]^{30+}$ core comprises a central distorted tetra-face-capped octahedron (Mn9-Mn18) either side of which are attached two vertex-sharing tetrahedra (Mn2–Mn8 and Mn19–Mn25), centred on Mn6 and Mn21. A pseudo two-fold axis passes through the direction defined by Mn13 and Mn17. The sixteen oxides all bridge in their familiar μ_3-mode with the ten hydroxides being of two types: four are μ_3-bridging (O10, O11, O14, O16) and found within the central face-capped octahedron and six are μ_2-bridging (O5, O6, O12, O15, O22, O23). The twenty deprotonated BTA ligands are of two types: four use all three nitrogens to bind three different Mn centres while the other sixteen ligands use only two nitrogens to bind to two different Mn centres, with the third nitrogen atom hydrogen-bonding to an adjacent MeOH, H_2O or OH ligand. The two protonated BTAH ligands are attached to Mn12, Mn13 and Mn14 and hydrogen-bond to each other, around the pseudo two-fold axis at the 'top' of the molecule. The BTA binding modes have all previously been seen in M^{2+} chemistry, but this is a rare example of BTA binding to a M^{3+} ion.[13]

The ten fluorides are all terminal with bond lengths in the range 1.800(8)–1.844(8) Å, and the Mn^{3+} ions display the expected Jahn–Teller elongations. All oxidation states were assigned using charge balance considerations, bond lengths and bond valence sum calculations. While the core of the molecule shows little disorder, the surrounding BTA and BTAH ligands show some disorder. Of the twenty two ligands, three show two clear components and thus the coordination environments of the Mn ions attached to these ligands have a degree of disorder associated with them.

Solid-state dc magnetic measurements were taken in the 1.8–300 K temperature range in a field of 1000 G. The room temperature $\chi_M T$ value of 80 emu K mol^{-1} is consistent with the spin-only value for twenty six non-interacting Mn^{3+} centers (78 emu K mol^{-1}). Below room temperature the value of $\chi_M T$ drops slowly to a value of approximately 20 emu K mol^{-1} at 20 K before dropping sharply to a value of 10 emu K mol^{-1} at 1.8 K. These data support an overall antiferromagnetic interaction

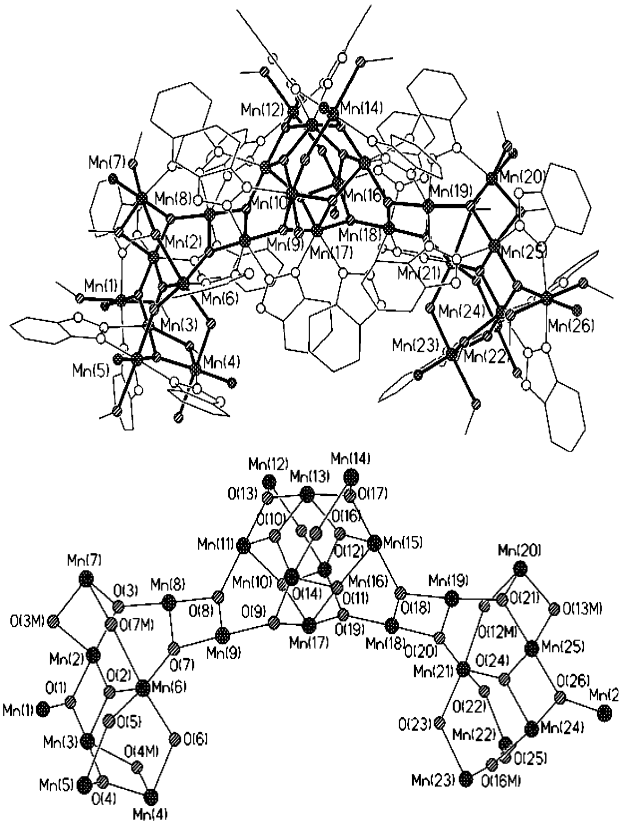

Fig. 1 The structure and core of complex **1**. Selected inter-atomic distances (Å): Mn^{3+}–F, 1.800–1.844(8); Mn^{3+}–N, 1.85–2.458(12); Mn^{3+}–O, 1.826–2.490(18).

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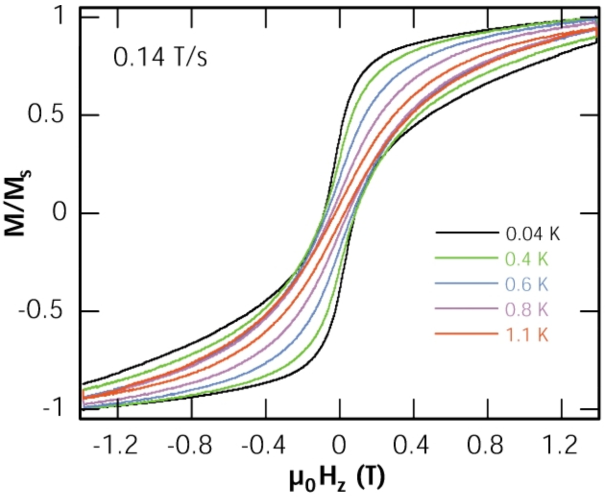

Fig. 2 Magnetization (M) of complex **1** plotted as fraction of maximum value M_s *vs*. applied magnetic field.

between the Mn^{3+} centres with a relatively low-spin ground state. To determine whether **1** is a SMM, low-temperature magnetic measurements were performed on single crystals using a micro-SQUID instrument which is equipped with three orthogonal field coils allowing the applied magnetic field to be turned in all directions. Hysteresis loops were measured on a single crystal with the field applied along the easy axis of magnetization. Below 1.2 K hysteresis loops are seen in magnetization *vs*. field studies whose coercivities increase with decreasing temperature, at sweep rates of 0.14 T s^{-1} (Fig. 2). The loops do not show the step-like features associated with quantum tunnelling of magnetization (QTM), and appear typical for a cluster with a distribution of energy barriers; the steps may be present but broadened out, as a result of the disorder associated with the crystal which gives a distribution of Mn^{3+} environments. This effect has been seen with other large metal cages.[14] Relaxation data at very low temperatures were determined from dc relaxation decay measurements; first a large dc field of 1.4 T was applied to the sample at 5 K to saturate the magnetization in one direction and the temperature lowered to a chosen value between 0.04 and 1.1 K. The field was then swept from 1.4 T to 0 T at a rate of 0.14 T s^{-1} and the magnetization in zero-field measured as a function of time. Fitting of these data to the Arrhenius Law gave an effective mean barrier for the reversal of magnetisation of approximately 15 K and a pre-exponential factor of $\tau_0 = 3 \times 10^{-9}$ s. The relaxation rate becomes temperature-independent below 0.2 K suggesting the presence of QTM in the ground state. More detailed magnetic measurements are underway to determine the precise nature of the ground state (S and D) of **1**. In summary, **1** represents the first example of a high nuclearity cage derived from MnF$_3$ and is a rare example of a Mn^{3+} cage stabilized by N-donor ligands. **1** also displays hysteresis and QTM at low temperature and is thus one of the largest molecules so to do.

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Notes and references

† Complex **1** analysed satisfactorily (Mn, C, H, N, F) as **1**·MeOH.

‡ *Crystal data*: $C_{151.50}H_{196}F_{10}Mn_{26}N_{66}O_{46.50}$, M = 5304.18, brown blocks, triclinic P1, a = 17.9570(10), b = 24.0865(14), c = 27.3871(16) Å, α = 98.907(2), β = 95.758(2), γ = 101.778(2)°, V = 11349.2(11) Å^3, T = 150(2), Z = 2, μ = 1.48 mm^{-1}, Synchrotron radiation (CLRC Daresbury Laboratory, Station 9.8, = 0.6867 Å) Bruker AXS SMART 1K CCD diffractometer,[15] narrow frame ω rotations, and corrected semi-empirically for absorption and incident beam decay (transmission 0.88–0.97) 37727 reflections collected, 23486 unique, (R_{int} = 0.0521) $2\theta_{max}$ = 40.14, 2581 parameters, R_1 = 0.0786 [13934 data with $I > 2\sigma(F)$], wR_2 = 0.2218 for 2581 parameters. CCDC 194440. See http://www.rsc.org/suppdata/cc/b2/b209445b/ for crystallographic data in CIF or other electronic format.

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