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New Routes to High Nuclearity Clusters: Fluoride-Based Octametallic and Tridecametallic Clusters of Manganese

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The reaction of MnF_3 with 5,6-dimethylbenzotriazole (Me_2BTAH) gives the $[Mn^{III}{}_8]$ complex $[Mn_8O_4(OMe)_2(Me_2BTA)_6F_8(Me_2BTAH)(MeOH)_8]$ and the $[Mn^{IV}{}_3Mn^{III}{}_{10}]$ complex $[Mn_{13}O_{12}(Me_2BTA)_{12}F_6(MeOH)_{10}(H_2O)_2]$. The octametallic species is an “intermediate” in the formation of the tridecametallic cluster.

Paramagnetic clusters of 3d transition metals are of current interest because they may act as single-molecule magnets (SMMs).[1] These molecules function as nanoscale magnetic particles as a result of the combination of a relatively large ground state spin (*S*) and an Ising (easy-axis) type of magnetoanisotropy (as gauged by the zfs parameter *D*). The barrier to magnetization relaxation is dependent on both *S* and *D* with the upper limits given by $S^2|D|$ and $(S^2 - 1/4)|D|$, for integer and non-integer spins, respectively. Thus it is important to find new molecules exhibiting large spins and/or large *D* values and to try to understand how clusters are assembled, in order to control cluster size and topology, and how the single-ion properties of a given cluster combine to give the total magnetic structure. Manganese clusters often display unusually large spin ground states, and negative *D* values arising from the presence of Jahn–Teller distorted Mn^{3+} ions.[2] The most successful way of making large clusters containing Mn^{3+} ions is through the use of the trinuclear species $[Mn_3O(O_2CR)_6L_3]^{0/+}$ or via the oxidation of simple Mn^{2+} salts in the presence of flexible organic bridging ligands.[3] Metal fluorides have been used to great effect in Cr carboxylate chemistry[4] and to a lesser extent in Fe chemistry,[5] but rarely in Mn cluster chemistry. We have been exploring the use of MnF_3 as an alternative precursor and recently reported the first example of a fluoride-based Mn cluster, [Mn26].[6] Herein we report the syntheses and structures of new octametallic and tridecametallic Mn clusters made from MnF_3.

Reaction of MnF_3 with 5, 6-dimethylbenzotriazole (Me_2BTAH) in boiling MeOH in air for 10 min leads to the formation of the complex $[Mn^{III}{}_8O_4(Me_2BTA)_6(OMe)_2F_8(Me_2BTAH)(MeOH)_8]$ **1** in good yield. Complex **1** (Figure 1) crystallizes, after 2 weeks, in the monoclinic space group $P2(1)/c$.[7] The core of **1** consists of a central $[Mn_4O_2]^{8+}$ butterfly unit (Mn3–Mn6), the body atoms of which (Mn3, Mn6) are also part of a peripheral $[Mn_3O]^{4+}$ triangular unit. The $[Mn_4O_2]$ butterfly is near planar with Mn4 and Mn5 approximately 10° above the “plane” defined by Mn3, Mn6, O8, and O12. The two peripheral $[Mn_3O]$ triangles are perpendicular to this plane, attached via an O^{2-} ion (O2, O11) forming a $[Mn_8O_4]^{16+}$ core. Two MeO^- (O1, O10) and two F^- (F7, F8) ions act as μ_2-bridges, the MeO^- bridging one side of the $[Mn_3O]$ unit and the F^- linking the $[Mn_3O]$ unit to the central $[Mn_4O_2]$ butterfly. The F^- bridges are asymmetric as, in each case, one Mn–F bond lies on a Jahn–Teller axis. The six Me_2BTA^- ligands all bond in a μ_2 fashion, and the remaining six F^- ions and eight MeOH molecules all are terminal. There is one protonated Me_2BTAH ligand present, bonded in a monodentate fashion to Mn7. It H-bonds to a terminal F^- ion on an adjacent molecule (e.g., N19–F6, 2.629 Å). The Mn^{3+} ions are all six-

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(7) Crystal data for **1**: $C_{68.5}H_{86}F_8Mn_8N_{21}O_{17}$, $M_r = 2067.10$, monoclinic, space group, $P21/c$ $a = 52.079(7)$ Å, $b = 15.469(2)$ Å, $c = 24.016(3)$ Å, $\alpha = 90.00°$, $\beta = 91.495(3)°$, $\gamma = 90.00°$, $V = 19341(4)$ Å^3, $T = 100(2)$ K, $Z = 8$, 109583 reflections collected, 39375 unique ($R_{int} = 0.1355$), $R(F) = 0.0741$ and $wR2 = 0.2055$ using 10703 reflections with $I > 2\sigma(I)$.

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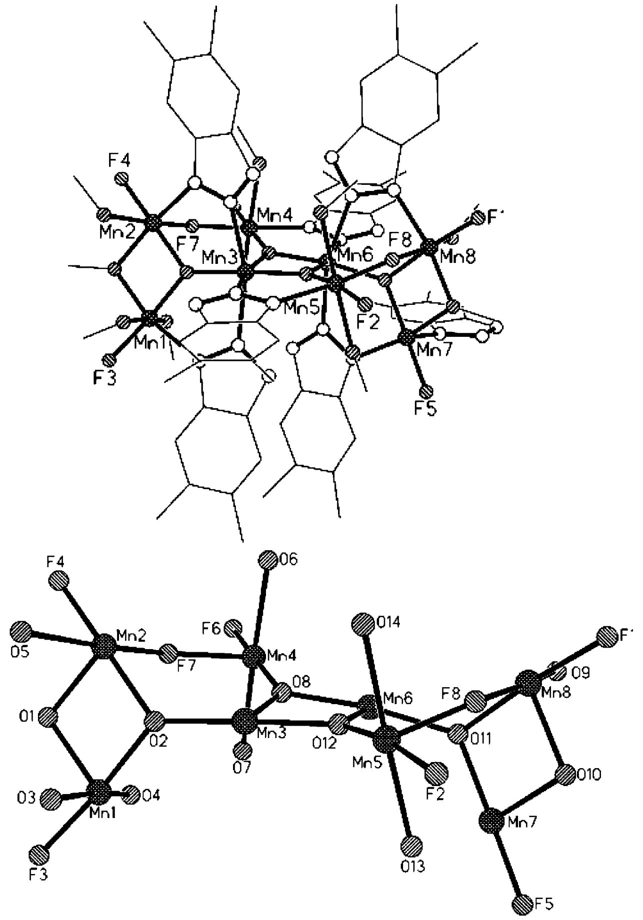

Figure 1. The structure of complex **1** (top) and side view of the core (bottom). Selected bond lengths (Å): Mn−O, 1.853(12)−2.315(11); Mn−N, 1.979(16)−2.255(17); Mn−F (bridging), 1.874(12)−2.184(12); Mn−F(terminal), 1.794(12)−1.847(12).

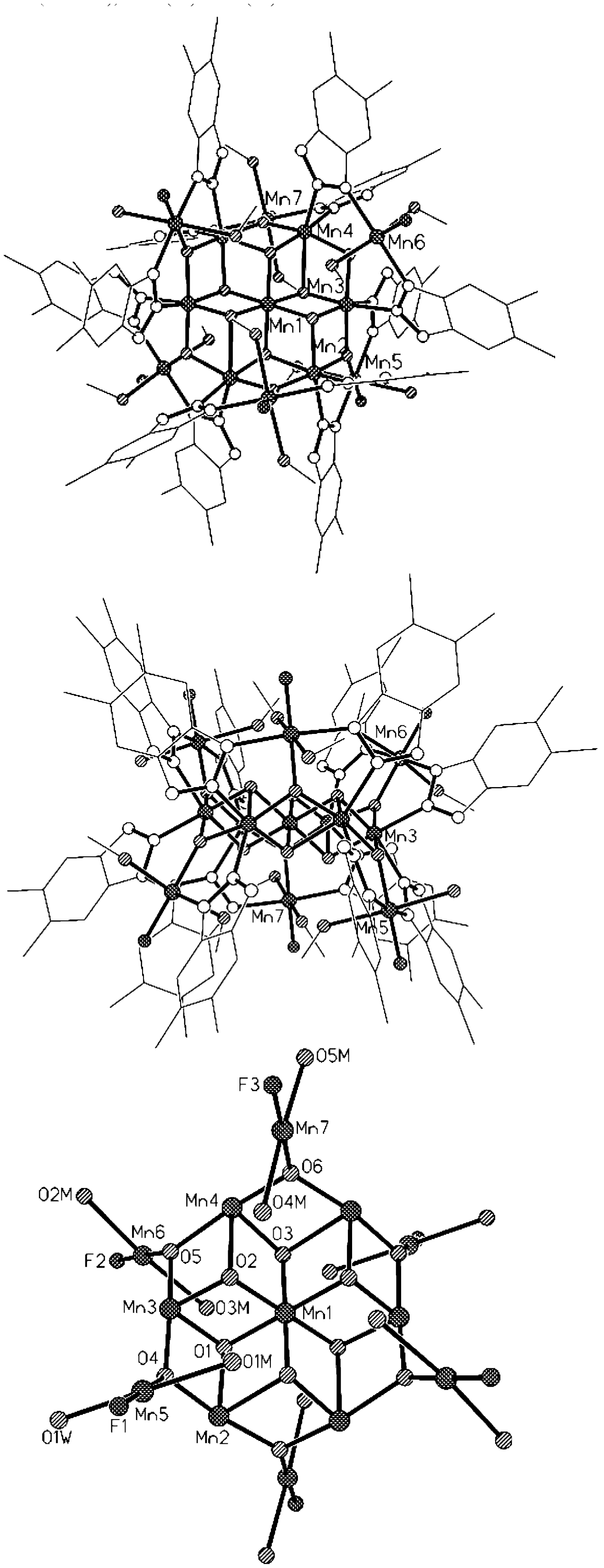

Figure 2. Structure of complex **2** (top), side view (middle), and core (bottom). Selected bond lengths (Å) Mn^{4+}−O, 1.865(5)−1.980(5); Mn^{4+}−N, 2.036(8)−2.047(8); Mn^{3+}−O, 1.854(6)−2.297(6); Mn^{3+}−N, 2.016(7)−2.228(8); Mn^{3+}−F, 1.796(6)−1.814(5).

coordinate and in distorted octahedral geometries, with one exception: Mn7 is 5-coordinate and square-based pyramidal with the nearest atom to the "vacant" coordination site the oxygen of a MeOH molecule bonded to Mn5 (O13−Mn7, 2.701 Å). All the Mn ions display the Jahn−Teller elongations expected of high-spin Mn^{3+} ions, although these are not all co-parallel. Assignment of the 3+ oxidation states was confirmed by BVS calculations and overall charge balance considerations. F analysis confirmed the presence of eight F^- ions.[8]

Repeating the reaction but this time boiling the methanolic solution for 20 min in air produces the related tridecametallic cluster $[Mn^{IV}_3Mn^{III}_{10}O_{12}(Me_2BTA)_{12}F_6(MeOH)_{10}(H_2O)_2]$ **2**. Centrosymmmetric complex **2** (Figure 2) crystallizes, after 2 weeks, in the triclinic space group $P\bar{1}$.[9] The core of **2** consists of a $[Mn^{IV}_3Mn^{III}_4O_{12}]$ hexagon centered on Mn1. The Mn^{4+} ions (Mn1, Mn3, Mn3A) form a linear $[Mn_3O_4]$ trimer through the center of the hexagon with the Mn^{3+} ions (Mn2, Mn4 and symmetry equivalents) attached on either side. The twelve O^{2-} ions are all μ_3-bridging and are of two types: six are bound to the central Mn^{4+} ion and link this ion to the outer six Mn ions of the hexagon. The remaining six O^{2-} ions bridge between the outer Mn ions of the centered hexagon and the remaining six Mn^{3+} ions (Mn5, Mn6, Mn7)

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[8] Elemental anal. Calcd (found) for **1**: C, 39.67 (39.95); H, 4.79 (4.03); N, 14.72 (14.96); F, 7.61 (8.11). Calcd (found) for **2**: C, 40.67 (39.83); H, 4.51 (4.12); N, 16.11 (16.58); F, 3.64 (3.84).

that are located, alternately, above and below the plane of the $[Mn^{IV}_3Mn^{III}_4O_{12}]$ core. The μ_2-Me_2BTA^- ligands are all deprotonated and link the Mn ions in the central hexagon to the Mn ions above and below this plane. The coordination of these six Mn ions is completed by a terminal F^- ion and either two MeOH molecules (for example, Mn6, Mn7) or one MeOH and one H_2O molecule (Mn5). All the Mn^{3+} ions show the expected Jahn−Teller elongations, although they are not co-parallel. Oxidation states were assigned using bond lengths, charge balance considerations, and BVS calculations.

1 is related to **2** and could be thought of as an "intermediate" in the formation of **2**. Both clusters appear to be constructed from $[Mn_3O]$ triangles and/or $[Mn_4O_2]$ butterfly units, each being extremely common building blocks in Mn cluster chemistry. In the same way the [Mn8] cluster can be thought of as an "intermediate" in the formation of the [Mn13] cluster: a $[Mn_8O_4]$ unit similar to that present in **1** can be seen three times in the core of **2**. For example, in **2**, the unit containing Mn1, Mn2, Mn3, and Mn5 forms the $[Mn_4O_2]$ butterfly unit with O1 and O4, with the peripheral $[Mn_3O]$ units sharing Mn2 and Mn3 with the butterfly and containing Mn4A, Mn7A, and O5, and Mn4, Mn6, and O5, respectively. The three fused $[Mn_8O_4]$ units all share the central Mn atom, Mn1. Each $[Mn_8O_4]$ then shares a $[Mn_4O_2]$ unit with its nearest neighbor with only one Mn ion in each unit unshared (e.g., Mn5, Mn7, and Mn6A). One major difference between the two clusters is the appearance of Mn^{4+} ions in **2**. As in most Mn cluster chemistry it is extremely unlikely that complexes **1** and **2** are the only ones present in solution at any one given time. Thus the oxidation of Mn^{3+} ions in **1** to Mn^{4+} ions in **2**, accompanied by the loss of F^- and MeO^- ions and the appearance of O^{2-} ions, is also likely to involve the deprotonation/protonation, structural rearrangements, and redox chemistry of other species present in solution.

The central $[Mn^{IV}_3Mn^{III}_4O_{12}]$ core of **2** is reminiscent of the hexagonal close-packed structure present in CdI_2 and the Mn^{4+} containing mineral lithiophorite,[10] and is similar to the cores found in $[Mn_7(OH)_3Cl_3(hmp)_9]^{2+}$,[11] $[Mn_7(OMe)_{12}(dbm)_6]$,[12] and the alkali metal containing species $[NaMn_6(OMe)_{12}(dbm)_6]^+$ [13] as well as larger molecules such as [Co24],[14] [Fe19],[15] [Mn16],[16] and [Mn21].[17] Complex **2** is only the second example of a tridecametallic Mn cluster after the "supercubane" reported in 1996.[18]

Complexes **1** and **2** represent only the second and third examples of manganese clusters derived from MnF_3 and are rare examples of Mn^{3+} and Mn^{4+}/Mn^{3+} clusters stabilized by N-donor ligands. The first example of a F^--based Mn cluster, [Mn26], was prepared via a "melt" reaction whereby the MnF_3 and organic ligand (benzotriazole, BTAH) mixture was heated to the melting point of BTAH, under an inert atmosphere. As the reaction proceeds, the MnF_3 dissolves in the organic ligand and the product can be extracted from the "melt" into a number of solvents. The reason for choosing a "melt" type of reaction was to overcome the relative insolubility of MnF_3 in common organic solvents. The formation of complexes **1** and **2** directly from hot MeOH solutions thus provides an alternative and potentially much simpler route from which to obtain high-nuclearity Mn clusters.

This suggests that MnF_3 is an excellent precursor for the synthesis of Mn^{3+} and Mn^{3+}/Mn^{4+} clusters and thus a potentially exciting precursor for the synthesis of new SMMs. The observation that two different Mn clusters, one being an "intermediate" in the formation of a second, can be isolated from the same reaction gives us some insight into how larger clusters form, and suggests that several different clusters can be made simply by changing reaction times and temperatures. One potential problem in this regard is the isolation of pure products and the avoidance of cross contamination, in this case, bulk material containing both **1** and **2**. Here, that can be avoided by careful control of reaction times. Bulk and single-crystal magnetic studies and multifrequency EPR experiments are currently underway and will be reported at a later date. Investigations into whether **1** can be directly converted to **2** are also in progress.

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Supporting Information Available: Crystallographic data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Crystal data for **2**: $C_{110.5}H_{155.5}F_6Mn_{13}N_{36}O_{27}$, $M_r = 3252.43$, crystal dimension = 0.06 × 0.04 × 0.01 mm^3, triclinic, space group, $P\bar{1}$, $a = 17.5604(13)$ Å, $b = 17.7334(13)$ Å, $c = 30.679(2)$ Å, $\alpha = 89.695(2)°$, $\beta = 73.548(2)°$, $\gamma = 60.850(2)°$, $V = 7901.1(10)$ Å^3, $T = 150(2)$ K, $Z = 2$, $\rho = 1.37$ Mg/m^3, 29859 reflections collected, 19051 unique ($R_{int} = 0.0426$), $R(F) = 0.0849$ and wR2 = 0.2400 using 13869 reflections with $I > 2\sigma(I)$. The data were collected on SRS at CCLRC Daresbury using a Bruker AXS SMART CCD area detector.

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