High-nuclearity, mixed-valence Mn$_{17}$, Mn$_{18}$ and {Mn$_{62}$}$_n$ complexes from the use of triethanolamine

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The use of both azide and triethanolamine, with or without the presence of carboxylate groups, has provided new Mn$_{17}$, Mn$_{18}$ and {Mn$_{62}$}$_n$ complexes with aesthetically-pleasing cage, layered, and linked-chain-type structures; two are also new single-molecule magnets.

One of the current challenges in inorganic chemistry is the synthesis and characterization of new molecular 3d metal polymeric clusters at moderate oxidation states. Reasons for this are varied, and not least among them is the aesthetic beauty that develops as the nuclearity of the clusters increases and the complexity of their molecular structures becomes apparent. From a more practical viewpoint, such large clusters can represent an alternative, ‘bottom-up’ route to nanoscale particles complementary to the traditional ‘top-down’ approach. An example is the discovery that molecular 3d-metal clusters can function as magnets, providing a ‘bottom-up’ approach to nanoscale magnetic materials, and such individual molecular species have come to be known as single-molecule magnets (SMMs). SMMs are molecules that display slow magnetization relaxation below a blocking temperature, $T_B$, due to a large ground state spin ($S$) combined with a large Ising (easy-axis) magnetoanisotropy (negative zero-field splitting (zfs) parameter, $D$). In addition, SMMs are true ‘mesoscale’ particles straddling the classical/quantum interface, and thus display quantum properties such as quantum tunneling of the magnetization vector (QTM) and quantum phase interference through the barrier. For all these reasons, SMMs have been proposed for various specialized applications, such as ultra-high density memory devices, spintronics, and quantum computing.

Although complexes displaying SMM behaviour are known for several metals, manganese cluster chemistry continues to be the most fruitful source, giving a wide range of Mn$_n$ nuclearities with $x$ having values up to 84, the latter being the largest known SMM. We have been developing new synthetic methods to Mn clusters of various nuclearities and structural types, and have recently been exploring the use of N$_3^-$ in higher oxidation state Mn chemistry in combination with various chelating/bridging ligands. From a magnetic viewpoint, the N$_3^-$ ion bridging in the 1,1-fashion (end-on) is one of the strongest ferromagnetic mediators in molecular magnetism, and thus it constitutes an attractive route to new high-spin molecules and SMMs.

In the present work, we report Mn reactions with azides and the potentially tetradentate (NO),O,OO) triethanolamine (teaH$_3$) chelating/bridging group, which has previously been found a useful route to high nuclearity non-azido and some lower nuclearity azido-based metal clusters. We have been targeting higher nuclearity Mn products by exploring the reactions between teaH$_3$, NaN$_3$ and various Mn reagents, with or without the co-presence of carboxylates. We herein report some results from this study, which has produced new mixed-valence Mn$_{17}$, Mn$_{18}$ and {Mn$_{62}$}$_n$ molecular species with tea$^-$/teaH$^-$/N$_3^-$ and tea$^3^-$/teaH$^-$/N$_3^-$/RCO$_2^-$ ligand combinations.

The reaction of Mn(ClO$_4$)$_2$·6H$_2$O, teaH$_3$, NEt$_3$, and NaN$_3$ in a 3 : 1 : 3 : 3 molar ratio in MeOH gave a dark brown solution from which was subsequently isolated [Mn$_{18}$O$_{11}$(OMe)(N$_3$)$_{12}$(tea)$_3$(teaH)$_3$(MeOH)] (1) in 65% yield. A very similar compound was recently reported by Murray and co-workers. A similar reaction, but with pivalate, between Mn(ClO$_4$)$_2$·6H$_2$O, NaO$_2$CCMe$_3$, teaH$_3$, NEt$_3$, and NaN$_3$ in a 2 : 2 : 1 : 1 : 2 ratio in MeCN/DMF (2 : 1, v/v) gave a similar dark brown solution from which was isolated [Mn$_{17}$NaO$_{10}$(OMe)$_2$(N$_3$)$_3$(tea)$_2$$(teaH)$_2$(MeOH)] (2) in 45% yield. Interestingly, when Mn(ClO$_4$)$_2$·6H$_2$O and MnO$_2$CCMe$_2$·4H$_2$O were combined in a 1 : 8 ratio in MeCN/MeOH (5 : 1, v/v), and treated with teaH$_3$ and NaN$_3$ in 1 : 4 ratio, the isolated product was now [Mn$_{19}$O$_{16}$(OMe)$_2$(N$_3$)$_3$(O$_2$CCMe$_3$)$_2$(tea)$_2$$(teaH)$_2$(MeOH)$_2$] (3) in 40% yield, where dea$^2^-$ is the dianion of diethanolamine. The partial transformation of teaH$_3$ to deaH$_2$ in 3 is attributed to metal-assisted -(CH$_2$)$_3$OH bond cleavage processes that are sometimes seen in 3d-metal cluster chemistry. The metal oxidation states and the protonation levels of O$_2$ are sometimes seen in 3d-metal cluster chemistry. The metal oxidation states and the protonation levels of O$_2$ are sometimes seen in 3d-metal cluster chemistry.
bridging azide groups. The core of I can be conveniently dissected into four layers, ABCD, of different sizes (Fig. 1, right) but all comprising fused [Mn₃O] triangular units: the MnIII monomeric layer A is the apex of the Mn₁₈ 'cone', linked to layer B which is a MnIII₃ triangle, thus giving a combined-layer AB tetrahedral topology; layer C is a large MnII₂MnIII₄ triangle comprising three corner-sharing MnII-MnIII₂ and MnIII₃ triangles connected to an additional, extrinsic Mn atom; and layer D consists of a MnIII₅ disk-like unit. Each layer is held together and linked to neighbouring layers by a combination of oxide, alkoxide, and µ₁,1,1 or µ₂,1,1 (end-on) azide ligands. The three tea⁴⁻ and teaH⁵⁺ groups are of four types: η¹⁻η¹⁻η¹⁻µ₁µ₃ and η¹⁻η¹⁻η¹⁻µ₃µ₄ for the former, and η¹⁻η¹⁻η¹⁻µ₄µ₃ and η¹⁻η¹⁻η¹⁻µ₃µ₄ for the latter, reflecting the bridging flexibility of the triethanolamine group.

The structure of 2 (MnII₂MnIII₁₂MnIV) consists of a Mn₁₇Na cage-like cluster (Fig. 2, top) with an irregular topology. The [Mn₁₇Na(µ₂-O)₂(µ₃-O)(µ₃-OH)₄(µ-OH)₂(µ₂-N₃)] core (Fig. 2, bottom) comprises seven [Mn₄(µ₂-O²⁻)] and one [Mn₂Na(µ₂-O¹⁻)] tetrahedra fused together and linked to one adjacent [Mn₂Na(µ₂-O¹⁻)] and two [Mn₃(µ₂-O²⁻)] triangles by common Mn vertices. The core can also be described as a central [Mn₃Na(µ₄-O²⁻)] tetrahedron fused to [Mn₄(µ₂-O²⁻)] and [Mn₄(µ₂-O²⁻)] cubanes at common atoms Mn(2) and Mn(9), respectively. All µ₂-O²⁻ ions in each cubane convert to a µ₄ mode and bridge seven adjacent Mn atoms, three of which (Mn2,5,7) are fused to the corresponding triangular subunits. The three tea⁴⁻ groups are each bridging up to six Mn atoms, acting as η¹⁻η¹⁻η¹⁻µ₁µ₆ and η¹⁻η¹⁻η¹⁻µ₄µ₅ and η¹⁻η¹⁻η¹⁻µ₃µ₄ ligands, the µ₄ mode being seen for a first time in the coordination chemistry of this group, while the only teaH⁵⁺ group is bridging in a η¹⁻η¹⁻η¹⁻µ₃ mode.¹⁴ Peripheral ligation is provided by ten η¹⁻η¹⁻µ₁, two η¹⁻η¹⁻µ₄ and an η²⁻η²⁻µ₄ Me₃CCO₂⁻ groups, as well as two terminal N₃⁻ ions and a terminal DMF molecule.

The structure of 3 (MnII₁₁MnIII₂₀) consists of Mn₂₈ units comprising a central Mn₄₈ subunit attached on each side to a Mn₂₄ rhombus and a Mn₃ triangle, with the metal atoms bridged by oxo, alkoxo, azido and acetato ions. These Mn₂₈ units are connected by linear [MnII₃(µCMe)(µO₂CMe)(µNa)] units into a 1D zig-zag chain. The structure is at first glance a polymer of Mn₃₁ units, but the Mn₃ bridge in a way that makes adjacent Mn₂₈ inequivalent, and complex 3 is thus best described as a chain of repeating Mn₂₈ units (Fig. 3) of formula [Mn₆₂O₃₈(OH)₂(OMe)₁₂(N₃)₈(O₂CMe)₄₆(tea)₄(dea)₄-Me₃CCO₂⁻]ₖ. Further, the 1D chains are linked by Mn(14)–N₃–Mn(18) inter-chain bridges, with the azide in an end-to-end mode, giving a 3D covalent network. The packing of the chains is provided in Fig. S11 (ESI†) which shows that (i) the linked-chains give sheets with a herring-bone pattern, and (ii) chains of adjacent linked-sheets are staggered so that when viewed along the chain axes a hexagonal close-packing is observed.

Solid-state dc (direct current) magnetic susceptibility (χₘ) data were collected on 1, 2, and 3-10MeCN in a 1 kG (0.1 T) field in the 5.0–300 K range. The data are plotted as χₘ vs. T in Fig. S3 (ESI†), and both 1 and 2 clearly have relatively large ground-state spin (S) values, whereas 3-10MeCN is strongly antiferromagnetically-coupled with χₘT heading for 0 cm⁻³ K mol⁻¹ at 0 K, indicating a dianagnetic ground state. χₘT for 1 increases from 66.53 cm⁻³ K mol⁻¹ at 300 K to 75.40 cm⁻³ K mol⁻¹ at 100.0 K, and then decreases to a plateau of ~60.50 cm⁻³ K mol⁻¹ at 15.0–8.0 K, before dropping to 58.93 cm⁻³ K mol⁻¹ at 5.0 K; the decrease at the lowest temperatures is assigned to Zeeman effects, zero-field splitting and/or weak intermolecular interactions. For 2, χₘT steadily decreases from 44.74 cm⁻³ K mol⁻¹ at 300 K to a plateau of

![Fig. 1](image1.png) **Fig. 1** Structure of 1 (left) and the four layers of its core (right). H atoms have been omitted for clarity. Colour scheme: MnIII yellow; MnIV blue; O red; N green; C grey.

![Fig. 2](image2.png) **Fig. 2** Structure of complex 2 (top) and its core (bottom). Colour scheme: MnIII yellow; MnII blue; MnIV olive; Na purple; O red; N green; C grey.

![Fig. 3](image3.png) **Fig. 3** Structure of the repeating {Mn₈} unit of polymeric complex 3. Colour scheme as in Fig. 1.
The susceptibility signals for both complexes were observed. Increase with increasing field sweep rate and decreasing exhibit hysteresis loops below temperature (Fig. 4), confirming 8.8 K and (solid lines in Fig. S4 and S5, ESI†) gave . The data were fit by matrix-diagonalization to a model that assumes only the ground state and S5 (ESI†), respectively. The data were fit by matrix-diagonalization to a model that assumes only the ground state and S0 values for high-nuclearity SMMs are becom-
ing more common, and can be assigned to differing factors such as relaxation contributions through low-lying excited states, distribution of molecular environments, and weak intermolecular interactions.

In conclusion, azide and triethanolamine groups together, with or without the presence of carboxylate anions, have provided three Mn clusters with interesting structures, namely a multi-layer pyramid (1), a closed cage (2) and a zig-zag chain (3), two of which (1 and 2) are also new members of the SMM family. These three complexes establish the potential of this reaction system to continue giving new molecular species with unprecedented nuclearities in 3d-metal coordination chemistry.

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Notes and references

§ Crystal data for 1:2CH2Cl2:4Et2O: C24H2c1Cl2Mn17Na3O36, . Mw = 3905.72, triclinic, space group P1, a = 15.3132(2) Å, b = 19.4122(11) Å, c = 21.422(2) Å, α = 69.092(2)°, β = 79.912(2)°, γ = 74.134(2)°, V = 5342.9(6) Å³, Z = 2, , = 1.924 g cm⁻³, T = 173(2) K, 3518 reflections collected, 23378 unique (R(0) = 0.0433), R1 [> 2σ(0)] = 0.0577, wR2 = 0.1433 (F², all data). CCDC 700137. Crystal data for 2: 5MeCN: C19H188Mn17Na3O36, Mw = 3453.68, orthorhombic, space group P2₁2₁2₁, a = 17.463(3) Å, b = 18.1443(4) Å, c = 46.054(7) Å, V = 46.054(7) Å³, Z = 4, , = 1.572 g cm⁻³, T = 173(2) K, 55542 reflections collected, 19027 unique (R(0) = 0.1192), R1 [> 2σ(0)] = 0.0972, wR2 = 0.2053 (F², all data). CCDC 700136. Crystal data for 3:26MeCN: C126H23Mn18Na3O36, Mw = 5365.54, monoclinic, space group P2₁/c, a = 35.759(4) Å, b = 14.890416(1) Å, c = 32.943(4) Å, β = 92.562(2)°, V = 1752(2) Å³, Z = 4, , = 2.034 g cm⁻³, T = 173(2) K, 69613 reflections collected, 22840 unique (R(0) = 0.1113), R1 [> 2σ(0)] = 0.0776, wR2 = 0.1874 (F², all data). CCDC 700138.

15 See the ESI†.

Fig. 4 Magnetization (M) vs. applied dc field (H) hysteresis loops for 1:2CH2Cl2:4Et2O (top) and 2:5MeCN (bottom) at the indicated temperatures. M is normalized to its saturation value (M₀).