Synthesis and Crystal and Molecular Structure of $(Et_4N)_2[Mn_{10}O_2Cl_8\{(OCH_2)_3CMe\}_6]\cdot 4MeOH\cdot 2H_2O$, a $Mn^{II,III}$ Mixed-valence Cluster with the Decametallate Core Geometry

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The reaction of $(Et_4N)_2MnCl_4$ with $MeC(CH_2OH)_3$ in acetonitrile in the presence of atmospheric oxygen yields the oxoalkoxomanganese cluster $(Et_4N)_2[Mn_{10}O_2Cl_8\{(OCH_2)_3CMe\}_6]\cdot 4MeOH\cdot 2H_2O$, a $Mn^{II,III}$ mixed valence species exhibiting the decametallate core geometry, $\{M_{10}O_2L_{26}\}$.

Polynuclear metal alkoxides have received significant contemporary attention because of their rich structural chemistry and as molecular precursors for oxide-based solids and other new materials.[1–3] The oxoalkoxometallate clusters represent an emergent subclass of compounds characterized by an equally diverse structural chemistry in which the oxo-groups serve in a multiple bridging capacity to anchor the polynuclear framework.[4–7] While complexes containing polymanganese oxo units are of considerable interest both as models for biological systems[8] and by virtue of their rich structural and magnetochemistry,[9] the oxoalkoxomanganese chemistry remains relatively unexplored, and little information is available in general about Mn^{II}-containing species.[8] In this paper, we report the synthesis and structural characterization of an anionic mixed valence $Mn^{II,III}$ cluster with the decametallate core geometry, $(Et_4N)_2[Mn_{10}O_2Cl_8\{(OCH_2)_3CMe\}_6]\cdot 4MeOH\cdot 2H_2O$ **I**.

The reaction of $(Et_4N)_2MnCl_4$ with an equivalent amount of $MeC(CH_2OH)_3$ in acetonitrile with vigorous stirring in a flask open to the air, followed by careful addition of methanol, yielded shiny black crystals of **I** in 50% yield.[†] The IR spectrum of **I** exhibits a strong band at 1040 cm^{-1}, characteristic of ν(C–O) of the ligand, and a feature at 347 cm^{-1} associated with ν(Mn–Cl).

The structure of the molecular anion of **I**,[‡] shown in Fig. 1(*a*), consists of the decametallate core $\{M_{10}O_{28}\}^4$ in which fourteen doubly bridging and four triply bridging oxo groups

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[†] Satisfactory elemental analyses.

[‡] *Crystal data* for $C_{50}H_{114}Cl_8Mn_{10}N_2O_{26}$: monoclinic $P2_1/n$, a = 11.769(3), b = 20.843(6), c = 15.891(3) Å, β = 95.96(2)°, V = 3877.0(17) Å^3, Z = 2, D_c = 1.707 g cm^{-3}. Structure solution and refinement based on 2064 reflections with $I_o \geqslant 3\sigma(I_o)$ converged at a residual of 0.0788. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

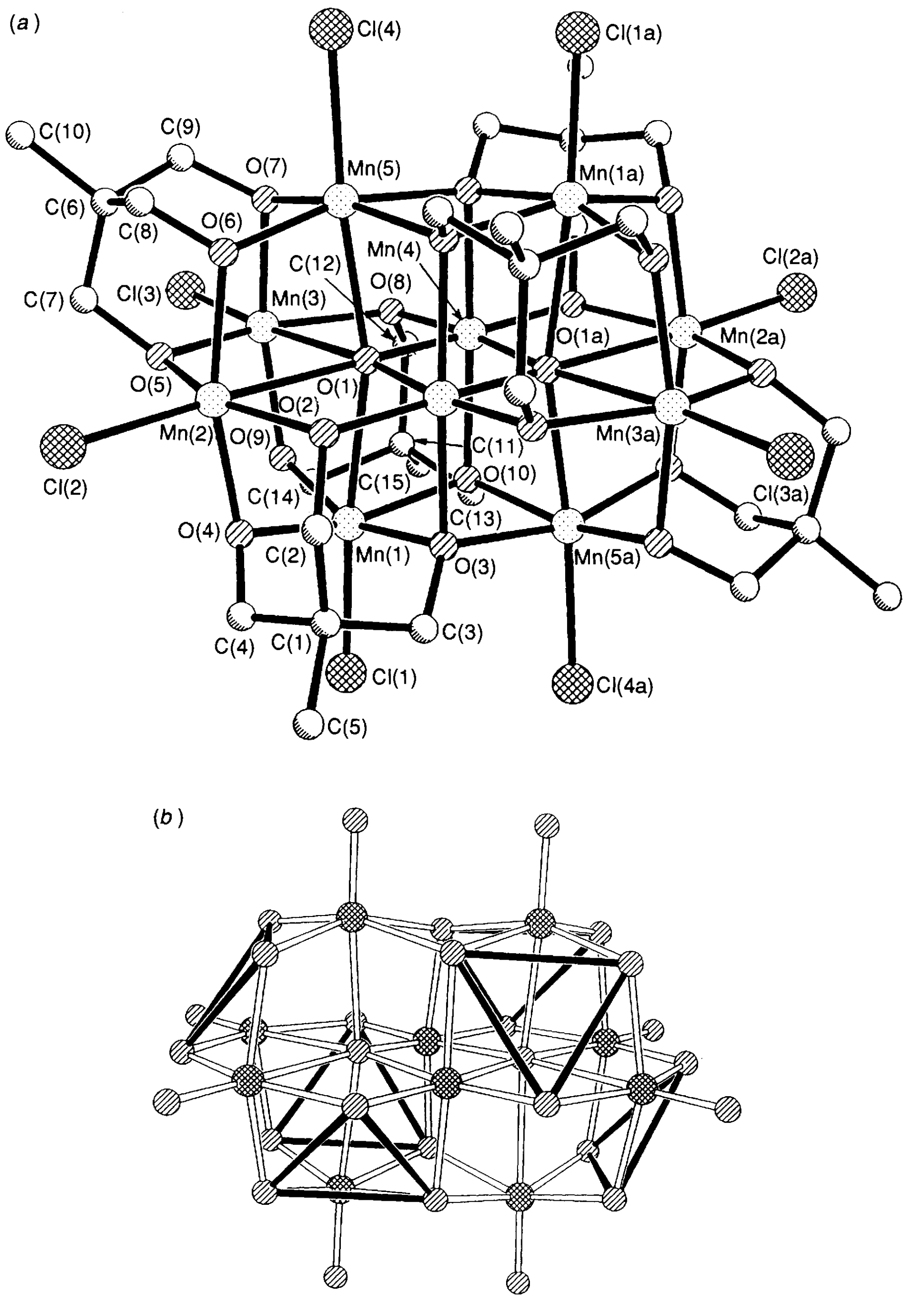

Fig. 1 (*a*) A view of the structure of $[Mn_{10}O_2Cl_8\{(OCH_2)_3CMe\}_6]^{2-}$, showing the atom-labelling scheme. The molecular anion lies on the crystallographic inversion centre. Bond length ranges (Å): Mn–Cl, 2.367(9)–2.460(12); Mn(1)–O(1), 2.54(2); Mn(2)–O(1), 2.48(2); Mn(3)–O(1), 2.52(2); Mn(4)–O(1), 1.95(2); Mn(5)–O(1), 2.38(2); Mn–O (μ_2-alkoxo): 1.92(2)–2.09(2); Mn–O (μ_3-alkoxo): 2.06(2)–2.25(2); Mn(4)···Mn(4a), 2.885(7); Mn···Mn (remainder): 3.200(9). (*b*) Schematic representation of the $\{M_{10}L_{28}\}$ core, highlighting the triangular cavities available for occupancy by the oxygen donors of the trisalkoxy ligands.

have been replaced by eighteen alkoxy donors from the six ligands and the eight terminal oxo-groups by eight chloride ligands. The geometry of the trisalkoxy ligand is such that it will preferentially adopt a bridging mode between three metal sites to give triangulo $[M_3\{(OCH_2)_3CMe\}]$ structural motifs, which condense to form larger aggregates. As shown schematically in Fig. 1(*b*), the decametallate core can accommodate up to six trisalkoxy ligands, which cap the triangular faces of the tetrahedral cavities formed by the fusion of metal octahedra in the core. Curiously, in the case of vanadium, cores with four and five trisalkoxy ligands, $[V_{10}O_{16}(tris)_4]^{4-}$ and $[V_{10}O_{13}(tris)_5]^{1-}$,[4] were isolated but not the fully substituted core. It is noteworthy that the structural core $\{Mn_{10}O_2\}$ contains multiply bridging oxo groups. This is a characteristic feature of the oxoalkoxo cluster class in which the oxo-groups appear to serve as structural anchors for the condensed cores.

The cluster charge is consistent with the presence of eight Mn^{III} and two Mn^{II} centres. Valence sum calculations[10] indicate that the two central Mn sites of the hexamanganese girdle of **I**, *i.e.* the Mn centres which are coordinated exclusively to oxygen donors, are Mn^{III} sites while the remaining eight sites exhibit intermediate geometries. The room temperature magnetism of 11.9 BM/Mn_{10} is substantially smaller than the expected value of 16.2 BM for high spin Mn(2 × II, 8 × III), indicative of the presence of an antiferromagnetic interaction between the Mn sites. The compound is EPR (electron paramagnetic resonance) inactive in the temperature range 140–293 K and exhibits only poorly resolved electrochemical features in acetonitrile.

Compound **I** is the second example of a high nuclearity Mn–oxo cluster that does not contain carboxylate ligands,[11] and a unique example of an anionic low-valent, high-nuclearity cluster. The relatively facile isolation of **I** reflects the role of the trisalkoxy ligand types in stabilizing $[M_3\{(OCH_2)_3CR\}]$ structural fragments that condense into larger aggregates, which often display classical polyoxoanion structural cores.[4,12]

This work was supported by a grant from the National Science Foundation (CHE 9119910).

Received, 1st September 1992; Com. 2/04676H

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