Novel Asymmetric Pentadentate *N*-(X-Substituted Salicylidene)-*N'*,*N'*-bis(2-hydroxyethyl)ethylenediamine Ligands afford the First Hexanuclear Manganese(III) Complexes

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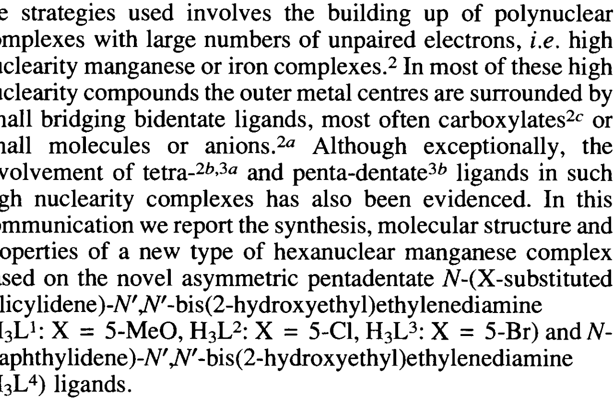
The topological arrangement of the metal centres in the first characterized hexanuclear manganese complexes, $[\{Mn^{III}{}_3L(O)(O_2CMe)(OMe)_3\}_2]\cdot 2solv$ [L = *N*-(X-substituted salicylidene)-*N'*,*N'*-bis(2-hydroxyethyl)ethylenediamine (X = 5-MeO, 5-Cl, 5-Br) and *N*-(naphthylidene)-*N'*,*N'*-bis(2-hydroxyethyl)ethylenediamine, solv = $2H_2O$ or MeOH], is unprecedented and shows that a variety of small bridging ligands including oxo, carboxylato and alkoxo anions may simultaneously cooperate with a dinucleating ancillary ligand to the building up of high-nuclearity manganese assemblies.

In recent decades the interest in oxo/hydroxo-bridged manganese complexes has increased because of their importance in biological systems.[1] More recently, nanoscale magnetic materials have been the focus of considerable research because they are expected to exhibit unusual magnetic properties and one of the strategies used involves the building up of polynuclear complexes with large numbers of unpaired electrons, *i.e.* high nuclearity manganese or iron complexes.[2] In most of these high nuclearity compounds the outer metal centres are surrounded by small bridging bidentate ligands, most often carboxylates[2c] or small molecules or anions.[2a] Although exceptionally, the involvement of tetra-[2b,3a] and penta-dentate[3b] ligands in such high nuclearity complexes has also been evidenced. In this communication we report the synthesis, molecular structure and properties of a new type of hexanuclear manganese complex based on the novel asymmetric pentadentate *N*-(X-substituted salicylidene)-*N'*,*N'*-bis(2-hydroxyethyl)ethylenediamine (H_3L^1: X = 5-MeO, H_3L^2: X = 5-Cl, H_3L^3: X = 5-Br) and *N*-(naphthylidene)-*N'*,*N'*-bis(2-hydroxyethyl)ethylenediamine (H_3L^4) ligands.

Monoacetylethylenediamine[4] **I** and *N*,*N*-bis(2-hydroxyethyl)ethylenediamine[5] **II** were prepared according to reported procedures as shown in Scheme 1. The Schiff- base condensation of **II** with aromatic aldehydes affording H_3L ligands with ONNOO donor sets was carried out in methanol, *in situ*, prior to the complexation reaction with manganese(II) acetate tetrahydrate in the presence of a methanolic solution of sodium methoxide [Na(OMe) : L : Mn ratio = 3 : 1 : 2] under strictly anaerobic conditions. The resulting yellow microcrystalline powders have the overall formulation $[Mn_2L(O_2CMe)(solv)]_n$ (L^1, L^3, L^4: solv = 0.5 MeOH; L^2: solv = 0.5 H_2O). IR spectroscopy indicates the presence of bridging acetates[6] ($\Delta = \nu_{asym} - \nu_{sym} = 112$–$128\ cm^{-1}$) while the identical and featureless $g \approx 2$ centred powder and dmf–toluene glass EPR spectra are characteristic of oligomeric manganese(II) species.[7] Attempts to grow single crystals of these oligomeric $[Mn^{II}{}_2L(O_2CMe)(solv)]_n$ species were unsuccessful due to their very low solubility in most solvents.



Scheme 1 The synthetic route to the novel asymmetric pentadentate *N*-(X-substituted salicylidene)-*N'*,*N'*-bis(2-hydroxyethyl)ethylenediamine (H_3L^1: X = 5-Cl, H_3L^2: X = 5-Br, H_3L^3: X = 5-MeO) and *N*-naphthylidene-*N'*,*N'*-bis(2-hydroxyethyl)ethylenediamine (H_3L^4) ligands

Carrying out these complexation reactions in the air afforded dark-brown solutions which yielded single crystals of **1** (L^1), **2** (L^2), **3** (L^3) and **4** (L^4), upon standing in closed vials for weeks. From the analytical and IR data, complexes **1–4** have the bulk formulation $[Mn^{III}{}_3L(O)(O_2CMe)(OMe)_3(solv)]$ (solv = MeOH for **1**, **3**, **4** and $2H_2O$ for **2**). Solution studies of complexes **1–4** and their oligomeric manganese(II) counterparts including electrochemistry and reactivity are in progress. The molecular structure determination of X-ray quality crystals obtained in the case of **1**[†] and **2**[‡] revealed the general hexanuclear formulation $[\{Mn^{III}{}_3L(O)(O_2CMe)(OMe)_3\}_2]\cdot 2solv$ [solv = MeOH (**1**), $2H_2O$ (**2**)]. The six manganese atoms in the polynuclear structure are distributed in two μ_3-oxo-centred trinuclear arrays related through an inversion centre situated in the middle of the O(9)–O(9') edge shared by the Mn(3) and Mn(3') coordination octahedra (Fig. 1). This structural arrangement may be viewed as a stacking of six edge-sharing coordination octahedra with the external Mn(1) [Mn(1')] coordination octahedra sharing one edge with each of the two adjacent Mn(2) and Mn(3) [Mn(2'), Mn(3')] octahedra, the intermediate Mn(2) [Mn(2')] coordination octahedra sharing one edge with each of the three adjacent Mn(1), Mn(2'), Mn(3) [Mn(1'), Mn(2), Mn(3')] octahedra and the central Mn(3) [Mn(3')] coordination octahedra sharing one edge with each of the four adjacent Mn(1), Mn(2), Mn(2'), Mn(3) [Mn(1'), Mn(2), Mn(2'), Mn(3)] octahedra. Alternatively, this hexanuclear manganese array may be described in terms of four face-sharing Mn_3O_4 incomplete cubane moieties.

Species **1** and **2** are the first hexanuclear manganese(III) complexes to be structurally characterized and the topological arrangement of their metal centres has not been previously observed either in iron or manganese chemistry. Among the seven hexanuclear manganese complexes already described, four are based on the trinuclear 'basic manganese carboxylates' and include two edge-sharing $Mn_4(\mu_4\text{-}O^{2-})$ tetrahedra with Mn^{III} atoms forming the shared edge and the four Mn^{II} atoms occupying the outer apices.[8] The six Mn^{II} atoms and six nitronyl-nitroxide radicals of the cyclohexamer reported by Rey and coworkers[9] define a 36-membered crown-shaped macrocycle, while the six Mn^{II} atoms of the *N*,*N*-diethylcarbamato complex described by Calderazzo and coworkers[10] are arranged at the apices of a puckered six-membered ring. In the fourth type of hexanuclear manganese compound described by

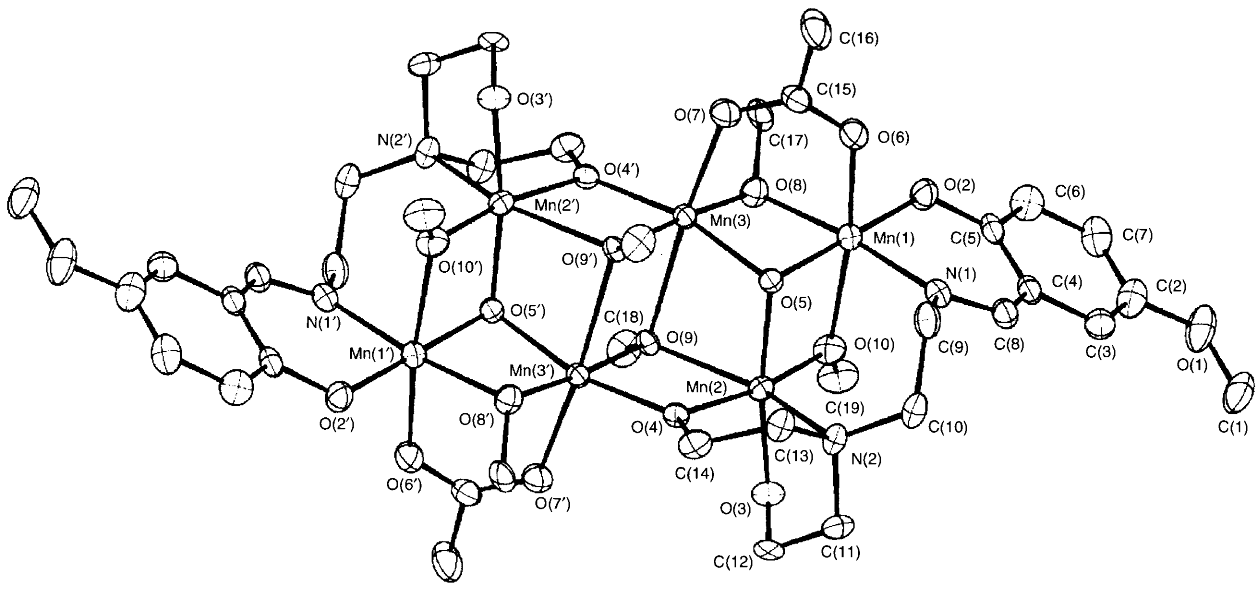


Fig. 1 Structure of **1** with atom labelling; hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Mn(1)–N(1) 2.060(5), Mn(1)–O(2) 1.870(4), Mn(1)–O(5) 1.885(4), Mn(1)–O(6) 2.142(4), Mn(1)–O(8) 2.025(4), Mn(1)–O(10) 2.141(4), Mn(2)–N(2) 2.336(5), Mn(2)–O(3) 1.868(4), Mn(2)–O(4) 2.020(4), Mn(2)–O(5) 1.939(4), Mn(2)–O(9) 2.218(4), Mn(2)–O(10) 1.895(4), Mn(3)–O(4) 1.935(4), Mn(3)–O(5) 1.908(4), Mn(3)–O(7) 2.145(4), Mn(3)–O(8) 1.920(4), Mn(3)–O(9) 2.387(4), Mn(3)–O(9′) 1.921(4), O(2)–Mn(1)–N(1) 90.3(2), O(2)–Mn(1)–O(6) 93.9(2), O(2)–Mn(1)–O(8) 95.4(2), O(2)–Mn(1)–O(10) 98.4(2), O(5)–Mn(1)–N(1) 92.7(2), O(5)–Mn(1)–O(6) 89.7(2), O(5)–Mn(1)–O(8) 81.3(1), O(5)–Mn(1)–O(10) 78.1(1), O(6)–Mn(1)–N(1) 93.0(2), O(6)–Mn(1)–O(8) 91.1(2), O(8)–Mn(1)–O(10) 89.5(2), O(10)–Mn(1)–N(1) 85.3(2), O(3)–Mn(2)–N(2) 82.5(2), O(3)–Mn(2)–O(4) 93.1(2), O(3)–Mn(2)–O(9) 105.4(2), O(3)–Mn(2)–O(10) 93.3(2), O(4)–Mn(2)–N(2) 78.0(2), O(4)–Mn(2)–O(5) 91.4(2), O(4)–Mn(2)–O(9) 72.0(1), O(5)–Mn(2)–N(2) 91.9(2), O(5)–Mn(2)–O(9) 82.5(1), O(5)–Mn(2)–O(10) 83.1(2), O(9)–Mn(2)–O(10) 99.5(2), O(10)–Mn(2)–N(2) 109.9(2), O(4′)–Mn(3)–O(7) 99.9(2), O(4′)–Mn(3)–O(8) 100.1(2), O(4′)–Mn(3)–O(9) 87.1(1), O(4′)–Mn(3)–O(9′) 80.6(2), O(5)–Mn(3)–O(7) 94.0(2), O(5)–Mn(3)–O(8) 83.5(2), O(5)–Mn(3)–O(9) 78.7(1), O(5)–Mn(3)–O(9′) 94.6(1), O(7)–Mn(3)–O(8) 91.0(2), O(7)– Mn(3)–O(9′) 93.3(2), O(8)–Mn(3)–O(9) 93.6(1), O(9)–Mn(3)–O(9′) 81.9(1), Mn(1)–O(5)–Mn(2) 102.6(2), Mn(1)–O(10)–Mn(2) 95.3(2), Mn(1)–O(5)–Mn(3) 98.0(2), Mn(1)–O(8)–Mn(3) 93.0(2), Mn(2)–O(5)–Mn(3) 111.4(2), Mn(2)–O(9)–Mn(3) 87.2(1), Mn(2)–O(4)–Mn(3′) 107.1(2), Mn(2)–O(9)–Mn(3′) 100.3(2), Mn(3)–O(9)–Mn(3′) 98.1(1). Non-bonding distances: Mn(1)···Mn(2) 2.986(1), Mn(1)···Mn(3) 2.862(1), Mn(2)···Mn(3) 3.178(1), Mn(2)···Mn(3′) 3.182(1), Mn(3)···Mn(3′) 3.267(2) (′ = 1 − *x*, − *y*, − *z*).

Weatherburn and coworkers,[11] the four $\mathrm{Mn^{III}}$ and the two $\mathrm{Mn^{IV}}$ atoms define a cross-shaped manganese array.

The magnetic susceptibilities of powdered samples measured in the range 300–2 K show a similar behaviour for complexes **1** and **2**. The effective magnetic moment for the six $\mathrm{Mn^{III}}$ ions of 11.3 μ_B at 300 K is lower than expected for six non-interacting $S = 2$ spin systems (12 μ_B) and decreases to a minimum value of 5.3 μ_B (**1**) [6.6 μ_B (**2**)] at 2 K. The interpretation of magnetic data for manganese(III) hexanuclear structures is difficult because the large number of pairwise interactions leads to the phenomenon of spin frustration. Moreover, the single-ion zero-field splitting (ZFS) of $\mathrm{Mn^{III}}$ is often of the same order of magnitude as the spin–spin exchange interaction which precludes any straightforward analysis of the data.[7] Both phenomena are expected to operate in this new type of hexanuclear structure: (*i*) the μ_3-oxo-centred trinuclear array is the textbook case of spin frustration[12] and as previously mentioned, **1** and **2** include two such triangular arrangements with distances of 2.986(1) (**1**), 2.945(4) (**2**) for Mn(1)···Mn(2), 2.862(1) (**1**), 2.831(4) (**2**) for Mn(1)···Mn(3) and 3.178(1) (**1**), 3.161(4) (**2**) for Mn(2)···Mn(3); (*ii*) although the distortion of the coordination octahedra is not purely axial due to constraints imposed by the polydentate ligand, significant axial elongations are evidenced along O(6)···O(10) [Mn(1)], N(2)···O(9) [Mn(2)] and O(7)···O(9) [Mn(3)] supporting the operation of quite large single-ion ZFS terms. The drop in effective magnetic moment observed between 13 and 2 K, that may be contrasted with the monotonous variation between 300 and 13 K, is a clear indication of the importance of these anisotropic interactions. Nevertheless, the magnetic interactions operating in this type of hexanuclear manganese(III) structure result in a bulk antiferromagnetic behaviour.

The reported synthesis and structural and physical properties of the oligomeric $[\mathrm{Mn^{II}}_2\mathrm{L(O_2CMe)(solv)}]_n$ and hexanuclear $[\{\mathrm{Mn^{III}}_3\mathrm{L(O)(O_2CMe)(OMe)_3}\}_2]\cdot 2\mathrm{solv}$ species clearly expand our knowledge of polynuclear manganese complexes, showing for the first time that a variety of small bridging ligands including oxo, carboxylato and alkoxo anions may simultaneously cooperate with a dinucleating ancillary ligand to the building up of high-nuclearity manganese assemblies.

We thank the CNRS for support, including a K. C. Wong post-doctoral fellowship to X. X.

Received, 7th July; Com. 5/04444H

Footnotes

† *Crystal data* for **1**: $\mathrm{C_{20}H_{35}Mn_3N_2O_{11}}$, $M_w = 644.3$, triclinic, space group $P\bar{1}$, $a = 10.103(7)$, $b = 11.488(6)$, $c = 12.866(6)$ Å, $\alpha = 72.49(4)$, $\beta = 73.35(5)$, $\gamma = 71.19(4)°$, $U = 1318(2)$ Å^3, $Z = 2$, $D_c = 1.62$ g cm^{-3}, μ(Mo-Kα) = 14.1 cm^{-1}, $T = 293$ K. Of 3234 data collected (Enraf Nonius CAD-4), Mo-Kα radiation ($\lambda = 0.7107$), $3 \leqslant 2\theta \leqslant 50°$, 2164 were used $[I > 3\sigma(I)]$. The structure was solved by direct methods and refined by full-matrix least squares methods (SHELXS 86[13] and CRYSTALS[14]). All non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as idealized contributions; $R = 0.033$ and $R' = 0.034$, with $w = 1$, $S = 1.8$ and 335 variables.

‡ *Crystal data* for **2**: $\mathrm{C_{18}H_{32}ClMn_3N_2O_{11}}$, $M_w = 652.7$, triclinic, space group $P\bar{1}$, $a = 10.882(1)$, $b = 12.338(4)$, $c = 10.417(2)$ Å, $\alpha = 103.70(2)$, $\beta = 100.91(2)$, $\gamma = 103.90(2)°$, $U = 1273.5(5)$ Å^3, $Z = 2$, $D_c = 1.67$ g cm^{-3}, μ(Mo-Kα) = 15.5 cm^{-1}, $T = 293$ K. Of 3141 data collected (Enraf Nonius CAD-4), Mo-Kα radiation ($\lambda = 0.7107$), $3 \leqslant 2\theta \leqslant 44°$, 1074 were used $[I > 3\sigma(I)]$. The structure was solved by direct methods and refined by full-matrix least squares methods as above. The manganese and chlorine atoms were refined anisotropically. All other non-hydrogen atoms were refined isotropically and hydrogen atoms were treated as idealized contributions; $R = 0.066$ and $R' = 0.069$, with $w = w'\,[1 - (\Delta F/6\sigma F_o)^2]^2$,

$S = 1.12$ and 162 variables [$w' = 1/\Sigma A_r \cdot T_r(x)$ with 4 A_r coefficients: 20.8, −29.6, 16.9, −5.4 and $x = F_c/F_{c\,max}$].

For both structures, atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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