

Synthesis and Crystal Structure of $[\text{Mn}^{\text{II}}(\text{H}_3\text{L})(\text{L})\text{Mn}^{\text{IV}}][\text{PF}_6]_3$ [$\text{H}_3\text{L} = N,N',N''\text{-tris-(2S)-2-hydroxypropyl-1,4,7-triazacyclononane}$]: a Mixed-valence Pendant-arm Macrocycle Dimer in which the Ligand Adopts Different Angular Geometries at the Two Metal Centres

Arafa A. Belal, Ian Fallis, Louis J. Farrugia, Norman M. Macdonald and Robert D. Peacock*

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK

Reaction of $N,N',N''\text{-tris-(2S)-2-hydroxypropyl-1,4,7-triazacyclononane}$ (H_3L) with MnCl_2 in neutral or slightly basic conditions affords $(\text{Mn}^{\text{II}}(\text{H}_3\text{L})(\text{L})\text{Mn}^{\text{IV}})[\text{PF}_6]_3$, a mixed-valence, hydrogen-bridged dimer in which the Mn^{IV} half has pseudooctahedral geometry and the Mn^{II} half has trigonal prismatic geometry.

Pendant-arm macrocycles are currently of considerable interest^{1,2} largely because of the ease of producing ligands with variable donor sets. The N_3 macrocycle, 1,4,7-triazacyclononane, for example, has been N -functionalised with at least eleven different kinds of 'arms'. The ligand $N,N',N''\text{-tris-(2S)-2-hydroxypropyl-1,4,7-triazacyclononane}$ (H_3L), which contains $-\text{OH}$ ligators, is particularly interesting because there is the possibility of it behaving as either an alcohol or an alkoxide donor. We report in this communication the structure of a mixed-valence $\text{Mn}^{\text{II}}, \text{Mn}^{\text{IV}}$ hydrogen-bridged dimer of H_3L in which the Mn^{II} and Mn^{IV} halves have different angular geometries.

We have recently described³ the preparation and structure of the Co^{III} complex of H_3L . The complex has a dimeric structure, $[\text{Co}(\text{H}_3\text{L})(\text{L})\text{Co}]^{3+}$, in which one of the Co^{III} atoms is coordinated by H_3L and one by the deprotonated alkoxide donor L , the two halves of the molecule being linked by hydrogen bridges. The dimeric structure persists in non-aqueous solvents, the bridging hydrogens being found³ at δ 14.6 in the ^1H NMR spectrum. In contrast to H_3L , pendant-arm macrocycles having phenol ligators [e.g. $N,N',N''\text{-tris-(2-hydroxybenzyl)-1,4,7-triazacyclononane}$], recently reported by Weighardt *et al.*,⁴ form monomeric complexes with trivalent metals in which the ligand is completely deprotonated. We have also prepared and determined the structures of complexes of H_3L with the divalent metals Mn^{II} ⁵ and Ni^{II} .⁶ In both cases the alcohol groups of the ligand retain their protons. The monomeric $[\text{Mn}(\text{H}_3\text{L})]^{2+}$ ion is oxidised by air in neutral or slightly basic aqueous solution to give a deep-red solution from which dark-red crystals of $[\text{Mn}(\text{H}_3\text{L})(\text{L})\text{Mn}][\text{PF}_6]_3$ **1** are obtained by metathesis.

The crystal structure† of **1** is shown in Fig. 1. The molecule is a hydrogen-bridged dimer and at first sight looks similar to $[\text{Co}(\text{H}_3\text{L})(\text{L})\text{Co}]^{3+}$. However, closer inspection shows that the two halves of the molecule have different geometries. One half, $[\text{Mn}(\text{H}_3\text{L})]^{2+}$, has bond lengths typical of $\text{Mn}^{\text{II}}-\text{O}$ and $\text{Mn}^{\text{II}}-\text{N}$ bonds and is therefore an Mn^{II} species; the other half has shorter bond lengths and is a Mn^{IV} species. Complex **1**

is thus a mixed-valence hydrogen-bridged dimer. The bond lengths of the Mn^{IV} part of the molecule are very similar to those of one of the few air stable Mn^{IV} complexes previously reported,⁷ the $[\text{Mn}_4(9\text{-aneN}_4)_4\text{O}_6]^{4+}$ ion, which has $\text{Mn}-\text{N} = 2.08 \text{ \AA}$ and $\text{Mn}-\text{O} = 1.79 \text{ \AA}$. The unusual Mn^{IV} oxidation state is required to balance the three $[\text{PF}_6]^-$ ions and is confirmed by magnetic moment measurements;⁸ μ_{eff} for the dimer is found to be $6.68 \mu_{\text{B}}$. The Mn^{II} and Mn^{IV} centres are weakly antiferromagnetically coupled; a reasonable fit to the data being obtained by using the Hamiltonian $H = -JS_1 \cdot S_2$ with $J = -1.0 \text{ cm}^{-1}$ and $g = 1.9$ ($S_1 = 5/2$, $S_2 = 3/2$).⁸ One possible reason why a Mn^{IV} species is formed instead of the more common Mn^{III} may be because of the extreme steric requirements of the ligand which would make the tetragonal Jahn-Teller distortion required by Mn^{III} very difficult to achieve.

As well as having different bond lengths, the two halves of the molecule have different angular geometries. The Mn^{IV} half has trigonally twisted pseudooctahedral geometry with a twist (ϕ)‡ of 10.9° similar to that in $[\text{Co}(\text{H}_3\text{L})(\text{L})\text{Co}]^{3+}$ ($\phi = 10.2^\circ$) and $[\text{Ni}(\text{H}_3\text{L})]^{2+}$ ($\phi = 20.0^\circ$). The Mn^{II} half of the dimer, however, has trigonal prismatic geometry ($\phi = 60^\circ$). This is shown clearly in Fig. 2 which depicts the two halves of the molecule looking down the C_3 axis. To our knowledge this

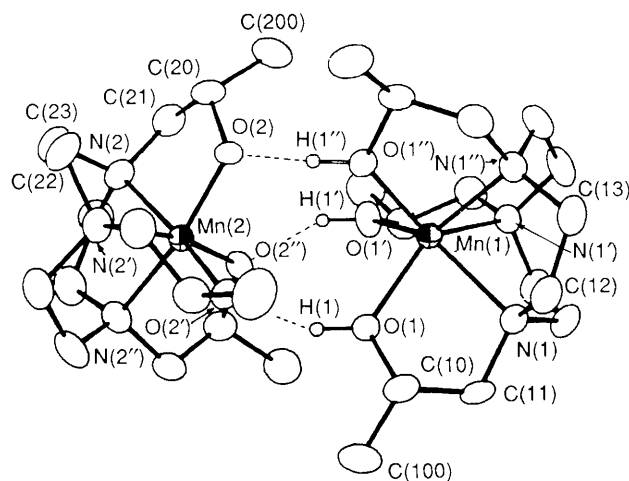


Fig. 1 Molecular structure and atomic labelling scheme for $[\text{Mn}(\text{H}_3\text{L})(\text{L})\text{Mn}][\text{PF}_6]_3$ **1**, with thermal parameters shown at the 20% probability level. Important bond lengths (\AA) and bond angles ($^\circ$) are: $\text{Mn}(1)-\text{N}(1)$ 2.251(5), $\text{Mn}(1)-\text{O}(1)$ 2.142(4), $\text{O}(1)-\text{H}(1)$ 0.906(4), $\text{N}(1)-\text{Mn}(1)-\text{N}(1')$ 78.6(2), $\text{O}(1)-\text{Mn}(1)-\text{O}(1')$ 91.8(2), $\text{N}(1)-\text{Mn}(1)-\text{O}(1)$ 77.0(2), $\text{Mn}(2)-\text{N}(2)$ 2.051(5), $\text{Mn}(2)-\text{O}(2)$ 1.857(4), $\text{O}(2)-\text{H}(1)$ 1.841(3), $\text{N}(2)-\text{Mn}(2)-\text{N}(2')$ 84.5(2), $\text{O}(2)-\text{Mn}(2)-\text{O}(2')$ 96.2(2), $\text{N}(2)-\text{Mn}(2)-\text{O}(2)$ 96.0(2).

† Crystal data for **1**: $\text{C}_{30}\text{H}_{63}\text{F}_{18}\text{Mn}_2\text{N}_6\text{O}_6\text{P}_3$, $M = 1149.6$, rhombohedral, space group $R\bar{3}$, $Z = 3$, $a = 10.472(1)$, $c = 36.637(7) \text{ \AA}$, $U = 3479.4(7) \text{ \AA}^3$, $D_c = 1.65 \text{ g cm}^{-3}$, $F(000) = 1773$, $\mu(\text{Mo-K}\alpha) = 7.4 \text{ cm}^{-1}$. The structure was solved by heavy atom methods and subsequent electron density difference synthesis, and was refined by full-matrix least-squares using 1365 observed, absorption-corrected data [$F_o > 3\sigma(F_o)$]. A total of 2198 unique data were measured on an Enraf-Nonius CAD4-F diffractometer with graphite monochromated $\text{Mo-K}\alpha$ X-radiation ($\lambda = 0.70169 \text{ \AA}$) using θ 2 θ scans. The final $R(R_w)$ values were 0.038(0.049) for 207 parameters, and $[\sigma^2(F_o)]^{-1}$ weights. Hydrogen atoms, except the OH atoms, were incorporated at fixed positions with $\text{C}-\text{H} = 1.0 \text{ \AA}$. The expected S conformation of the chiral C atoms was confirmed by refining the inverted configuration which converged to a higher residual of 0.040(0.053) and also by refinement of η , the anomalous scattering factor, which refined to a value of 0.74 for the S configuration. 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.

‡ The angle ϕ is defined as the angle of twist away from an exactly staggered arrangement of ligators as viewed down the C_3 axis. Thus ϕ is 0° for octahedral geometry and 60° for trigonal prismatic geometry.

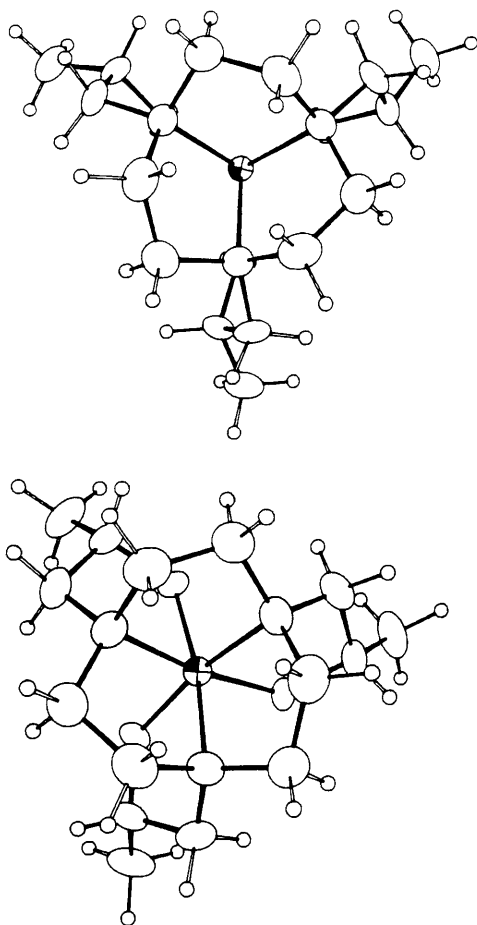


Fig. 2 View of the two halves of **1** looking down the C_3 axis: top $[Mn^{II}(H_3L)]^{2+}$; bottom $[Mn^{IV}(L)]^+$

is the only case where a metal complex of a pendant-arm ligand based on [9]aneN₃ forms a trigonal prismatic complex. {The molecule with the largest trigonal distortion from octahedral symmetry reported previously⁹ is $[Fe(L')]$, $L' = N,N',N''$ -tris-carboxymethyl-1,4,7-triazacyclononane, which

has $\phi = 34.8^\circ$. It is not at all clear why the trigonal prismatic geometry is favoured by the $[Mn(H_3L)]^{2+}$ unit. The N–Mn–O angle of the five-membered exocyclic chelate rings is contracted by about 20° compared to the pseudooctahedral structure and as a consequence the exocyclic rings are more strained. In the monomeric complex $[Mn(H_3L)][MnCl_4]$,⁵ the $[Mn(H_3L)]^{2+}$ ion adopts a structure half-way between pseudooctahedral and trigonal prismatic ($\phi = 37.4^\circ$) but the issue is complicated by extensive hydrogen bonding between the OH groups of the cation and the $[MnCl_4]^{2-}$ anion. One interesting consequence of the trigonal geometry is that the [9]aneN₃ ring adopts the δ conformation which is the opposite chirality to that adopted in the Mn^{IV} half of **1** (and in the other complexes of H₃L whose structures have been determined).

The cyclic voltammogram of **1** shows two reductions (0.54 V, reversible, and -0.06 V, quasi-reversible, vs. normal hydrogen electrode, NHE) and an irreversible oxidation (1.65 V vs. NHE). The reductions, are tentatively assigned to the processes $Mn^{II}, Mn^{IV} \rightarrow Mn^{II}, Mn^{III}$ and $Mn^{II}, Mn^{III} \rightarrow Mn^{II}, Mn^{II}$, respectively. The irreversible oxidation is probably $Mn^{II}, Mn^{IV} \rightarrow Mn^{IV}$ monomeric species.

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