X-Ray Crystal Structure and Some Properties of a Tetranuclear, Mixed-valence Manganese Complex of a Macrocyclic Ligand

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The complex $[Mn_2{}^{II} Mn_2{}^{III}(L)O(MeCOO)_3Cl(MeOH)]\cdot 3MeOH$ has been prepared and structurally characterised; the complex is a possible model for the manganese centre of Photosystem II.

The structure and function of the water-splitting manganese centre of Photosystem II are currently under intense investigation.[1] Extensive studies on the biological system suggest that the active site contains four coupled manganese ions[2] but the geometry of the complex, the oxidation levels involved, and the mechanism of action remain uncertain. In part, this has been due to the lack of suitable model systems, the properties of which could be compared with those of the natural system. Hence recently, several tetranuclear manganese complexes,[3] in various different oxidation states and geometries, have been prepared and studied. Here we report the synthesis and structural characterisation of a mixed-valence, macrocyclic $Mn_2{}^{II} Mn_2{}^{III}$ complex. A similar mixed-valence configuration has been suggested[4] for the S_{-1} state of Photosystem II.

The complex $[Mn_2{}^{II}Mn_2{}^{III}(L)O(MeCOO)_3Cl(MeOH)]\cdot 3MeOH$ was obtained from reaction of 2,6-diformyl-4-methyl phenol with 1,5-diamino-3-hydroxypentane dihydrochloride (neutralised with KOH) in the presence of manganese(II) acetate, in a methanol–ethanol mixture. Brown crystals suitable for *X*-ray study were obtained by recrystallisation from a mixture of methanol and ether.

The structure† of the complex is shown in Figure 1; Figure 2

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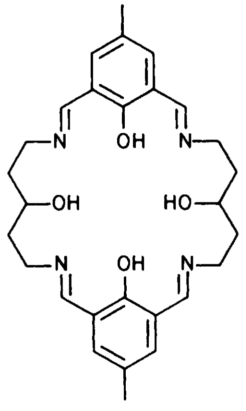
† *Crystal data:* brown, monoclinic, dimensions 0.64 × 0.52 × 0.16 mm^3 from methanol/ether (1 : 5), $C_{38}H_{57}ClMn_4N_4O_{15}$, $a = 16.224(4)$, $b = 12.862(2)$, $c = 22.061(4)$ Å, $\beta = 96.57(2)°$, $U = 4573(2)$ Å^3, space group $P2_1/c$, $Z = 4$, $\mu = 11.62$ cm^{-1}. Data were collected at 170 K on a Nicolet R3m four-circle diffractometer using graphite monochromated Mo-K_α radiation. 6336 unique reflections were collected in the range $4 < 2\theta < 47°$ and 4544 having $I > 3\sigma(I)$ were used in the structural analysis. The structure was solved by direct methods and gave a final $R = 0.0497$ and $R_w = 0.0699$. All programmes used in data reduction and structure solution are contained in the SHELXTL (Version 4.0) package.[5] Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



H_4L

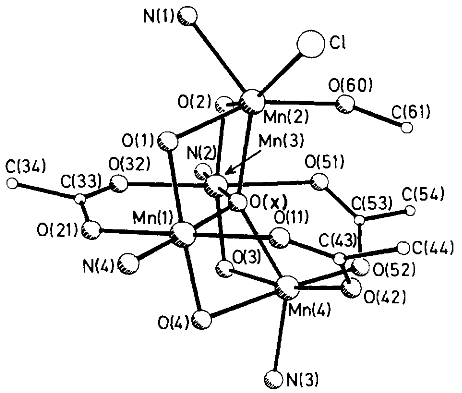


Figure 1. The $[Mn_2^{II}\,Mn_2^{III}(L)O(MeCOO)_3Cl(MeOH)]$ complex.

shows the co-ordination spheres of the metal ions. In contrast to a tetra-copper(II) complex[6] prepared from H_4L, the macrocycle is non-planar. The mean planes of the two phenol rings are inclined to each other at an angle of 38.5°. The alcohol and phenol groups of the macrocycle are all deprotonated and each bridges two manganese ions, so that the ligand is octadentate. The co-ordination spheres of the metal ions are completed by: a central oxo-anion (bound to each manganese ion), three bridging acetate groups, a chloride ion, and a methanol molecule. Three other methanol molecules are present in the asymmetric unit but these are not co-ordinated to the metal complex.

Mn(1) and Mn(3) have very similar co-ordination and geometry; each is six-co-ordinate and approximately octahedral, co-ordinated to the macrocycle through one imine nitrogen, one phenoxy oxygen, and one alkoxy donor. In addition, each is bound to two acetate groups (*trans* to one another) and to the oxo ion, O(x). Five of the six ligands bound to Mn(1) or Mn(3) are bridging and bind to at least one other manganese ion. Mn(2) and Mn(4) are also six-co-ordinate but have less regular geometry than the other metal ions. Mn(4) has the same donor set as Mn(1) or Mn(3) but the acetate groups are *cis* rather than *trans*. In the co-ordination sphere of Mn(2) the acetate groups are replaced by a chloride anion and a methanol group. The manganese centres have a 'butterfly' configuration; each manganese atom has two relatively short (but non-bonding) interactions with other metal ions and one longer separation. A similar pattern is indicated by EXAFS studies on the biological system.[8]

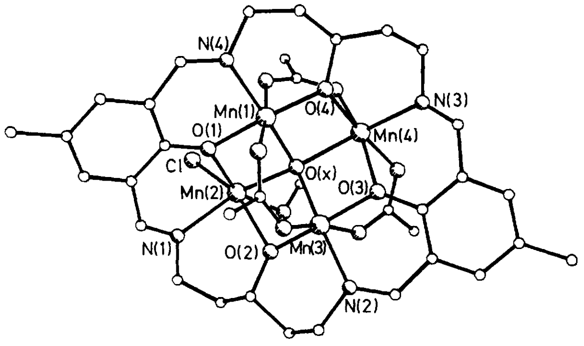


Figure 2. The co-ordination spheres of the manganese ions. Selected interatomic distances (Å) and angles (°). Mn(1)-Mn(2) 3.158(1), Mn(1)-Mn(3) 3.442(1), Mn(1)-Mn(4) 3.016(1), Mn(2)-Mn(3) 3.169(1), Mn(2)-Mn(4) 4.151(2), Mn(3)-Mn(4) 3.059(1), Mn(1)-O(x) 1.906(4), Mn(2)-O(x) 2.248(4), Mn(3)-O(x) 1.901(4), Mn(4)-O(x) 2.144(4), Mn(1)-O(1) 1.944(4), Mn(2)-O(1) 2.197(4), Mn(3)-O(3) 1.942(4), Mn(4)-O(3) 2.297(4), Mn(1)-N(4) 2.027(5), Mn(2)-N(1) 2.216(5), Mn(3)-N(2) 2.010(5), Mn(4)-N(3) 2.177(5), Mn(1)-O(4) 1.878(4), Mn(2)-O(2) 2.191(4), Mn(3)-O(2) 1.871(4), Mn(4)-O(4) 2.247(4), Mn(1)-O(31) 2.196(4), Mn(1)-O(41) 2.283(4), Mn(3)-O(32) 2.157(4), Mn(3)-O(51) 2.407(4), Mn(2)-Cl 2.463(3), Mn(2)-O(60) 2.215(4), Mn(4)-O(42) 2.116(4), Mn(4)-O(52) 2.140(4), Mn(1)-O(x)-Mn(2) 98.6(2), Mn(1)-O(x)-Mn(3) 129.4(2), Mn(2)-O(x)-Mn(3) 99.2(2), Mn(1)-O(x)-Mn(4) 96.1(2), Mn(2)-O(x)-Mn(4) 141.9(2), Mn(3)-O(x)-Mn(4) 98.1(2).

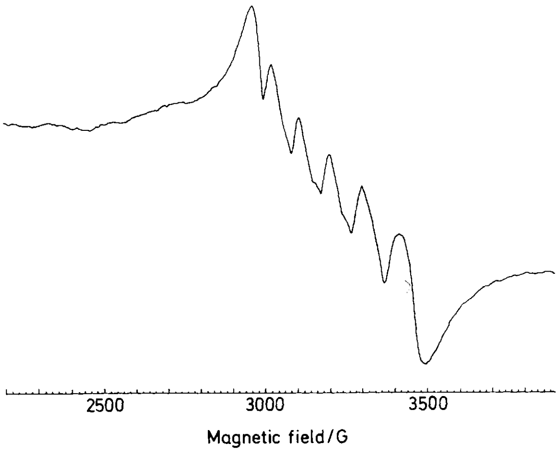


Figure 3. E.s.r. spectrum of the complex in dimethylformamide at −160 °C. 1 G = 10^{-4} T.

The stoicheiometry of the complex requires that the average oxidation level for the manganese atoms is 2.5. The structural data provide strong evidence for the localisation of the charges; bond distances about Mn(1) and Mn(3) are very similar and are significantly shorter than equivalent bonds to Mn(2) or Mn(4). Similar distinctions in bond lengths have been observed recently in other Mn^{II} Mn^{III} mixed-valence systems.[4,9] Consequently, we assign the original +2 oxidation state to Mn(2) and Mn(4), whereas Mn(1) and Mn(3) have been oxidised to the +3 level. The most likely oxidising agent for this process is molecular oxygen and this may also be the source of the oxo-ligand. A reduction of molecular oxygen to hydroxide in a tetranuclear copper(I) complex has been reported recently.[10] However, hydroxide bound in square planar Cu^{II} and Ni^{II} complexes of L and related ligands seems likely to have originated from water.[6,7]

The presence of electronic interactions between the metal ions is indicated by preliminary magnetic measurements; the mean magnetic moment falls from 5.12 μ_B/Mn at 300 K to 4.56 μ_B/Mn at 93 K.‡ Both these values are significantly below the mean spin-only moment expected in the absence of any coupling (5.41 μ_B/Mn). More detailed magnetic studies are underway. Figure 3 shows the e.s.r. spectrum of the complex in a dimethylformamide glass at 113 K; there is no observable spectrum at room temperature. The main feature is the 6-line spectrum expected for Mn^{II}, possibly the result of some dissociation in polar solvent. However, there is a broad underlying spectrum which may be due to the tetramer and which may be improved if spectra can be obtained at lower temperatures and at Q band.

The facile oxidation of two manganese centres suggests that other oxidation levels should be accessible for this complex. It is expected that the presence of a macrocyclic ligand bound to all four metal ions will assist in maintaining the structure intact in solution and through chemical changes. Hence it may be possible to synthesise Mn_4L complexes in a variety of oxidation states for comparison with the manganese centre of Photosystem II.

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‡ 1 $\mu_B \approx 9.27 \times 10^{-24}$ A m^2.