Crystallographic Characterisation of a Possible Model For Photosystem II

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An X-ray crystal study of $[Mn(3,5,Cl\text{-}salen)(H_2O)_2]_2(ClO_4)_2$ [3,5,Cl-salen = *N,N'*-3,5-dichloro(salicylidene)-1,2-diaminoethane] reveals it to be a hydrogen-bonded di-aquabridged dimer; a combination of the steric bulk of the ligand and a hydrogen bonding system creates a coordination cleft which can allow the approach of *p*-benzoquinone and water photolysis to occur on irradiation with visible light (no such photolysis occurs when sterically bulky 2,5-*tert*-butyl-*p*-benzoquinone is employed).

The photosynthetic oxidation of water occurs within photosystem II (PSII), located in the thylakoid membranes of plants and cyanobacteria.[1] It has been established that for high rates of oxygen evolution from the oxygen evolving centre (OEC) four manganese ions are required although their exact functional role is still in doubt.[2] As a result of this many models of the OEC have been proposed containing mono-,[3] di-[2,4,5] and multi-nuclear manganese centres in a variety of oxidation states (II–IV).[2,4,6] Following the simple dinuclear model for the OEC in PSII proposed by Calvin,[7] our strategy has been to produce manganese(III) complexes of tetradentate Schiff base ligands (with an N_2O_2 donor set) with non-coordinating counterions to enable water to coordinate to the metal centre. These models have proved to be remarkably successful in terms of their photolytic activity,[8,9] and have demonstrated that alternative manganese water-splitting systems, other than the natural system, are available. We now present the crystallographic characterisation of a manganese(III) complex which resembles the di-aqua-bridged model proposed by Calvin[7] as the active site in PSII; we also propose a mechanism for the evolution of oxygen based on this structure.

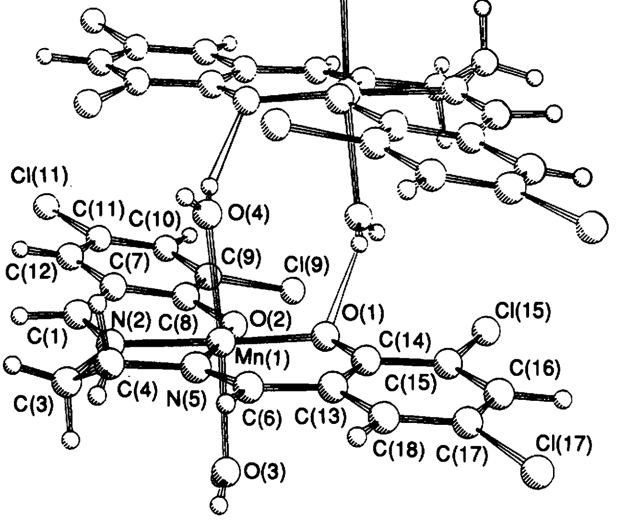

Fig. 1 The crystal structure of $[Mn(3,5,Cl\text{-}salen)(H_2O)_2]_2(ClO_4)_2$

Crystals† of $[Mn(3,5,Cl\text{-}salen)(H_2O)_2]_2(ClO_4)_2$ [3,5,Cl-salen = *N,N'*-3,5,dichlorobis(salicylidene)-1,2-diaminoethane] were prepared by a modification of the method developed by Boucher and Coe,[11] by the reaction of the disodium salt of the ligand (0.25 g, 0.55 mmol) with manganese(II) perchlorate (0.20 g, 0.55 mmol) in ethanol (50 cm^3). After stirring for 5 days in the presence of air, the solution was filtered and the solid discarded and the filtrate evaporated to dryness. Slow evaporation of an isopropyl alcohol solution of this solid produced crystals suitable for single crystal X-ray diffraction studies which proved to be the hydrogen bonded di-aqua-bridged manganese(III) dimer $[Mn(3,5,Cl\text{-}salen)(H_2O)_2(ClO_4)_2$, Fig. 1.

The structure comprises a planar tetradentate Schiff base tightly bound to manganese(III) centre *via* Mn–N bonds of 1.963(4) and 1.973(4) Å and Mn–O bonds of 1.889(3) and 1.871(3) Å.

The distortion in the *z*-axis towards the capping water molecules may be partially attributed to the Jahn–Teller effect, as would be expected for a d^4 ion, resulting in longer Mn–O distances of 2.220(5) and 2.272(5) Å. The manganese(III) centres are linked *via* an array of hydrogen bonds between the phenoxy oxygen atoms of the ligand and one of the capping water molecules. This produces a hydrogen bonded di-aqua-bridged structure which we previously pro-

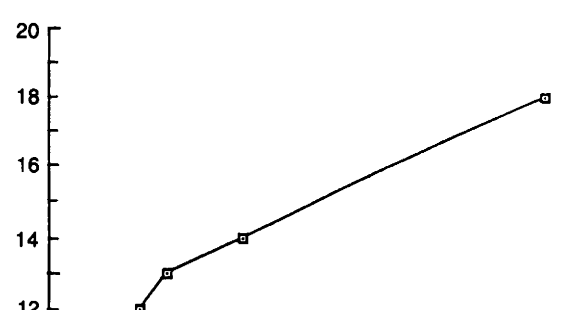

Fig. 2 Graph of $\%O_2$ dissolved in solution *vs.* time for $[Mn(3,5,Cl\text{-}salen)(H_2O)_2]_2(ClO_4)_2$

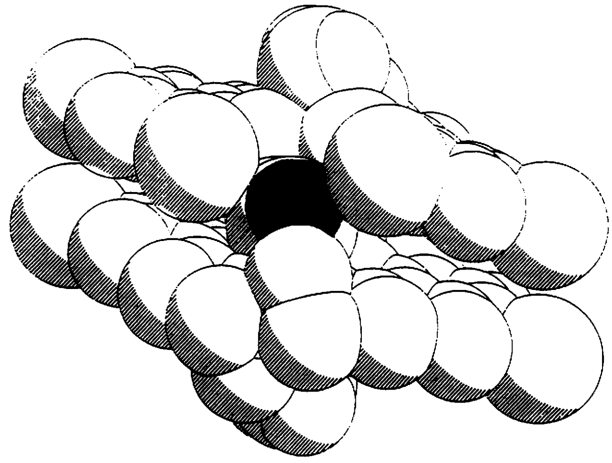

Fig. 3 Space-filling diagram of $[Mn(3,5,Cl\text{-}salen)(H_2O)_2]_2(ClO_4)_2$ with the cavity protons (H_A) shaded black

posed to be the structure of these manganese(III) Schiff base complexes,[8] with a Mn···Mn separation of 5.070(2) Å. The hydrogen bonding along with the steric bulk of the ligands, creates a coordination cleft in which the bridging aqua groups are situated. The combined effect of hydrogen and π-bonding between pairs of molecules could possibly result in the integrity of this dimer remaining in aqueous solution.[‡] An aqueous solution of the compound in the presence of *p*-benzoquinone evolves dioxygen when irradiated with a 500 W tungsten bulb. Fig. 2 shows that dioxygen is generated by the complex, which, in the absence of *p*-benzoquinone, remains unchanged. No change in the evolution of dioxygen is observed when the photolysis experiment is performed in anhydrous ethanol, indicating that it is from the water coordinated to manganese that the dioxygen is evolved.

Photolysis[§] of an aqueous solution of *p*-benzoquinone leads to slow loss of *p*-benzoquinone and to the formation of a mixture of dihydroquinone and 2-hydroxy-*p*-benzoquinone without the generation of molecular oxygen. This is due to the generation of OH· radicals after abstraction of H· from water by photoexcited *p*-benzoquinone.[12,13] Awad and Anderson[14] suggested that the most energetically favourable step for the generation of dioxygen from our complexes would be the abstraction of H· from μ-coordinated water by photo-excited *p*-benzoquinone.

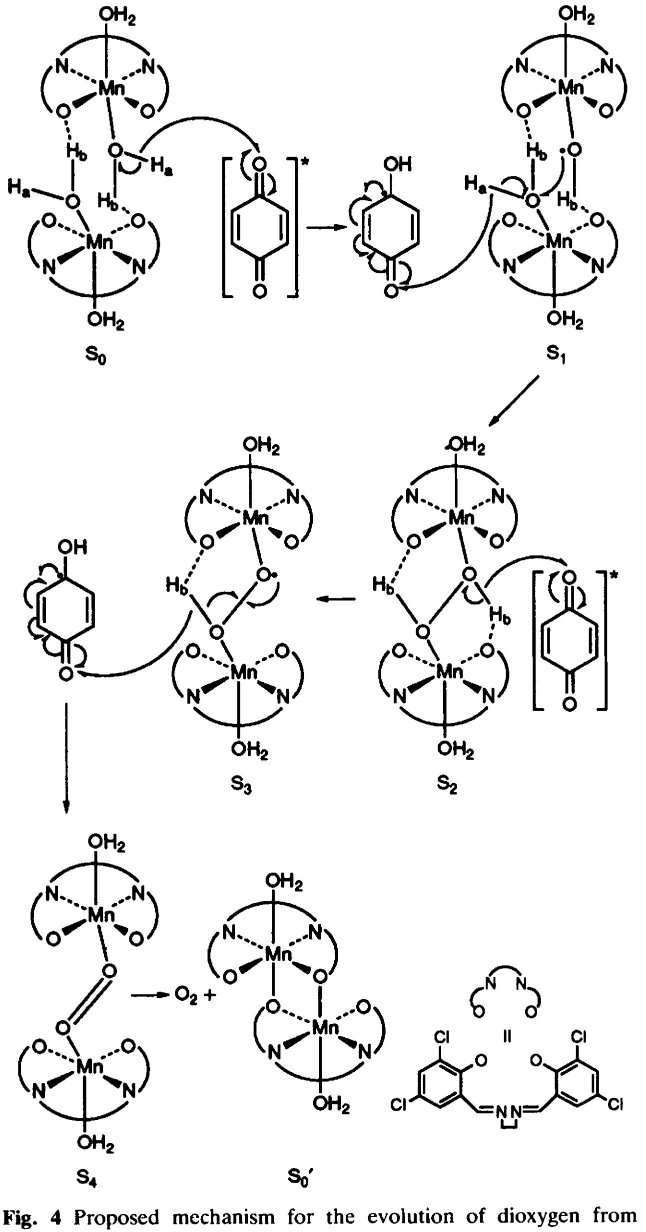

Fig. 4 Proposed mechanism for the evolution of dioxygen from manganese(III) Schiff base complexes

This is due to the potency of photo-excited *p*-benzoquinone in stripping H· radicals from water and the relative stability of OH· radicals in aqueous solution.[12,13] We also believe this to be the case, as a space-filling diagram of $[Mn(3,5,Cl\text{-}salen)(H_2O)_2]_2(ClO_4)_2$, Fig. 3, clearly shows that the μ-aqua-bridges are in a cleft with one hydrogen pointing outwards from each side of the dimer (shaded). This coordination cleft enables photo-excited *p*-benzoquinone to enter the cleft and abstract the H· radical. These two protons have been labelled H_A in Fig. 4, a mechanism for the evolution of dioxygen. The abstraction of the H_A protons generates OH· radicals; however, the fact that 2-hydroxy-*p*-benzoquinone is not observed in the UV–VIS spectrum indicates that they are stabilised by the manganese complex, presumably due to their position in the coordination cleft. This postulation is supported by the fact that no dioxygen is evolved when 2,5-*tert*-butyl-*p*-benzoquinone is used rather than *p*-benzoquinone. The greater steric requirement of this H· acceptor prevents it from entering the coordination cleft, and shows that it is not from the sterically unhindered capping water that dioxygen is evolved. This observation further supports the existence of aqua-bridged dimers in solution. We propose that this process results in the formation of a μ-hydroperoxy-bridged intermediate which would produce some geometrical change enabling the strongly hydrogen-bonded hydrogens H_B to be abstracted by excited *p*-benzoquinone by the same process as the H_A protons. This process generates a transient dioxygen bridged manganese complex, which almost instantaneously decomposes producing dioxygen and a μ-phenoxy bridged manganese(III) dimer, S_0', a dimer that we have previously isolated from a photolysis study.[9] These proton abstractions result in concurrent one electron oxidations of the manganese complex mimicking the Kok S states of PSII.[15]

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Footnotes

[†] *Crystal data*: for $C_{16}H_{14}O_8N_2Cl_5Mn$, monoclinic, $P2_1/c$ (No. 14), a = 12.349(4), b = 12.880(4), c = 14.165(5) Å, β = 106.66(2)°, V = 2158(2) Å^3, Z = 4, D_c = 1.829 g cm^3, Mo-Kα radiation (λ = 0.71069 Å), 233 K, Siemens R3mv diffractometer with graphite monochromator structure solutions were obtained by direct methods (DIRDIF).[10] Final residual factors were R_F = 0.045, R_w = 0.041.

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.

[‡] A Referee suggested that osmometry measurements be performed to establish the presence of a dimer in solution. Unfortunately, insufficient solubility in water rendered this measurement impossible. However, in AR methanol and using diazobenzene as a reference, a value of 920 was obtained after two days equilibration (calc. monomer, 594.5; dimer 1189), indicating that in this solvent, at least, the complex species in solution is predominantly dimeric.

[§] Photolysis experiments were performed as previously reported on a 25 mg sample of $[Mn(3,5,Cl\text{-}salen)(H_2O)_2]_2(ClO_2)_2$ in 500 cm^3 of water at 25 °C.[8] Oxygen electrode readings were recorded as % dissolved oxygen where 100% corresponds to a fully saturated aqueous solution at 25 °C (6 cm^3 O_2 dm^{-3}) and 0% corresponds to no dissolved oxygen.

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