The Visible Light Induced Rearrangement of a Manganese(III) Complex of an Unsymmetrical Tetradentate Schiff's Base Ligand, 4-[2-(2-hydroxyphenylmethyleneamino)ethylamino]pent-3-en-2-one, to a Manganese(III) Complex of the Symmetrical Ligand salen†

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Visible light irradiation of [{Mn(L)(H_2O)}$_2$](ClO_4)$_2$·4H_2O, which contains the tetradentate unsymmetric Schiff's dianionic ligand 4-[2-(2-hydroxyphenylmethyleneamino)ethylamino]pent-3-en-2-one, results in the formation of the dimeric [{Mn(salen)(H_2O)}$_2$](ClO_4)$_2$·H_2O, which contains the symmetrical dianionic Schiff's base ligand *N,N'*-bis(salicylidene)ethylenediaminato; the X-ray crystal structure of the latter complex is reported.

It is well established that manganese plays a central role in some biological systems, *e.g.* in a superoxide dismutase[1] and an azide insensitive catalase;[2] of greater importance is that manganese is essential for the oxidation of water to O_2 in the photosynthetic process,[3,4] having been found to be associated with the water-oxidising complex (WOC) in all O_2-evolving photosynthetic organisms so far studied. Moreover, no other metal has been found to reactivate lost O_2-evolution activity in reconstructed complexes deficient in manganese.

There is currently a great deal of interest in synthesising models of this system based on high nuclearity manganese complexes, *viz.* Mn_4,[5] Mn_6,[6] Mn_9[7] but, we[8] and others[9–14] have examined binuclear systems in an attempt to mimic the water photolysis action of photosystem II (PPSII) of the green plant. We have succeeded in generating molecular oxygen and reducing *p*-quinone to hydroquinone by visible irradiation of aqueous solutions of [{Mn(saltn)(H_2O)}$_2$](ClO_4)$_2$·2H_2O.†[8] Recently a quantum mechanical study of our work has been published by Awad and Anderson.[15]

We have sought to extend our work to involve unsymmetrical tetradentate ligands bound to high-valent manganese. Although such ligands are rare, they are not unknown and have been complexed with oxovanadium(IV),[16] copper(II),[17,18] nickel(II)[17,19] and cobalt(III).[19]

We have prepared the unsymmetrical Schiff's base ligand H_2L in quantitative yield by the reaction of 4-[2-(aminoethyl)-amino]pent-3-en-2-one with salicylaldehyde (Scheme 1).[20]

Elemental analyses and ^1H NMR data point to high purity of this yellow solid. The dark-brown manganese(III) complex of this ligand, [{Mn(L)(H_2O)}$_2$](ClO_4)$_2$·4H_2O was prepared in good yield according to the method of Boucher and Coe,[21] and gave satisfactory elemental analyses.

The complex exhibits a broad ν(OH) band in the Nujol mull IR spectrum centred at 3450 cm^{-1}, and ν(C=N) appears at 1630 cm^{-1}; a broad unsplit absorption centred at 1120 cm^{-1} is indicative of ionic perchlorate. Its FAB mass spectrum shows evidence for the presence of ions at *m/z* 299 corresponding to [Mn(L)], which is further proof that the structure of the unsymmetrical ligand has been retained in the complex. The presence of the ligand L in the complex was further confirmed by a comparison of the X-ray powder diffraction profile of the complex and that for the salen complex; they are significantly different. The compound exhibits μ_{eff} = 5.0 μ_B at room temperature. This value is within the range expected for an Mn^{III} octahedral complex. Studied over the temperature range 77–292 K, a plot of 1/X_m *vs.* *T* gives a straight line which almost goes through the intercept, evidence for no antiferromagnetic interaction.

Prior to our normal photolysis experiment involving an aqueous solution of the complex plus *p*-benzoquinone, we simply irradiated an aqueous solution of only the complex with a 300 W tungsten lamp for 6 h. After irradiation and upon standing copious quantity of small dark crystals formed (yield *ca.* 40%). To our surprise these proved to be crystals of a dimeric manganese(III) complex containing the well known symmetrical salen ligand, [{Mn(salen)(H_2O)}$_2$](ClO_4)$_2$·H_2O (Fig. 1).‡ This remarkable rearrangement (1) is, to our

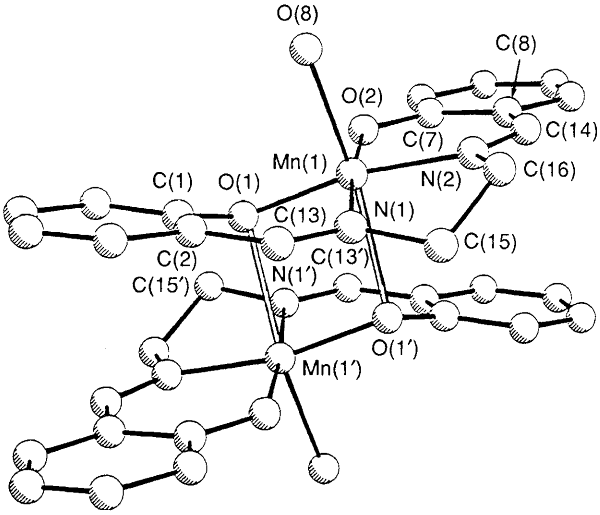
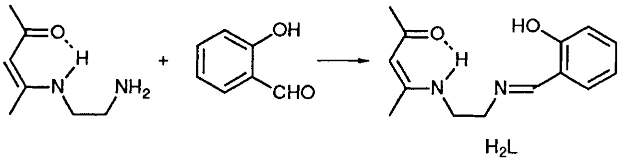


Fig. 1 Structure of the [{Mn(salen)(H_2O)}$_2$]$^+$ dimer; perchlorate anions, water of crystallisation and hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°): Mn(1)–O(1) 1.891(3), Mn(1)–O(2) 1.866(3), Mn(1)–O(8) 2.208(3), Mn(1)–N(1) 1.975(4), Mn(1)–N(2) 1.972(4), Mn(1)–O(1') 2.490(3), Mn(1) · · · Mn(1') 3.361(2), O(1)–Mn(1)–O(2) 94.2(1), O(1)–Mn(1)–O(8) 94.3(1), O(1)–Mn(1)–N(1) 90.5(1), O(1)–Mn(1)–N(2) 168.3(1), O(1)–Mn(1)–O(1') 80.7(1), where ' denotes −*x*, −*y*, −*z*.



Scheme 1

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† H_2salen = *N,N'*-bis(salicylidene)ethylene diamine; H_2saltn = *N,N'*-bis(salicylidene)-1,3-diaminopropane.

‡ *Crystal Data*: $C_{16}H_{18}ClN_2MnO_8$, *M* = 456.72, monoclinic, $P2_1/n$, *Z* = 4, *a* = 7.206(3), *b* = 13.382(3), *c* = 19.399(1) Å, β = 94.84(1)°, *V* = 1864(1) Å^3; D_c = 1.628 Mg m^{-3}, μ(Cu-Kα) = 7.58 mm^{-1}. A Rigaku AFC5R diffractometer, Cu-Kα radiation (λ = 1.541 78 Å) in ω–2θ scan mode; 3159 reflections recorded (0 < θ < 120°). Lorentz-polarisation, decomposition and absorption corrections were applied. The structure was solved by direct methods and refined by full-matrix least-squares to a *R* = 0.054 and R_w = 0.069 for 2348 observed reflections with $F > 3\sigma(F)$. 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.

knowledge, unique, and, since in other studies of metal complexes of this[17,19] and similar unsymmetrical ligands[17–19] the integrity of the unsymmetrical ligand appears to be maintained, our observations would seem to suggest that this represents another demonstration of the chemical potency of manganese(III) in the presence of visible light.

$$\mathrm{Mn^{III}(L)} \rightarrow \mathrm{Mn^{III}(salen)} \qquad (1)$$

It is well known that Schiff's base condensations are subject to hydrolysis in acid or basic conditions to reform the carbonyl and amine precursors and it may well be that manganese(III) catalyses this process also. However, in order to form salen from L, hydrolysis of both imine groups must occur and, although the metal ion may act as a template for the formation of salen from the hydrolysis fragments, it is difficult to understand why the newly formed $[\{\mathrm{Mn(salen)(H_2O)}\}_2]^{2+}$ does itself then not undergo hydrolysis. A control experiment in anhydrous methanol does not result in the production of $[\{\mathrm{Mn(salen)(H_2O)}\}]^{2+}$, implying that water is necessary for the ligand rearrangement to occur. The rearrangement does not occur immediately, but needs several hours of irradiation.

The crystals of $[\{\mathrm{Mn(salen)(H_2O)}\}_2](\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$ obtained from the rearrangement reaction contain globules of an oily material, presumably fragments of the original ligand, but we have been unable to identify these so far.

Fig. 1 shows how each $[\mathrm{Mn(salen)H_2O}]^+$ moiety is linked to its neighbour across a crystallographic inversion centre by two shared phenoxy oxygen atoms. Although the bridging Mn–O bonds of 2.490(3) Å are weak, they complete a distorted octahedron about each manganese. The crystal packing scheme includes a water of crystallisation which hydrogen bonds the coordinated water and a perchlorate anion. A further hydrogen bond between the coordinated water and on adjacent phenoxy oxygen completes the structure. The two manganese atoms are separated by only 3.361(2) Å.

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