Structural and Spectroscopic Characterization of the Manganese(IV) Schiff Base Complex Mn(saladhp)$_2$ (saladhp = 2-salicylideniminato-1,3-dihydroxy-2-methylpropane

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The first Mn^{IV} Schiff base complex to be structurally characterized by *X*-ray crystallography, Mn^{IV}(saladhp)$_2$ (**1**) (saladhp = 2-salicylideniminato-1,3-dihydroxy-2-methylpropane) has been synthesized and its physical properties reported (E_{pc} = −460 mV *vs.* Ag/AgCl and a small axial zero field splitting parameter); the reported data are of potential importance to the understanding of manganoenzymes.

The chemistry of the higher oxidation states of manganese, such as Mn^{IV}, is poorly understood and represents a fertile area for studying the biological chemistry of manganese. Manganese is an essential component of photosynthetic oxygen evolution,[1] most likely participating as the oxidant of water in equation (1). In this case, the oxygen evolving

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (1)$$

complex contains four manganese ions which are most likely associated, forming two binuclear centres or a large cluster.[2] Manganese also catalyses the reduction of hydrogen peroxide to water as in the pseudocatalase isolated from *Lactobacillus*

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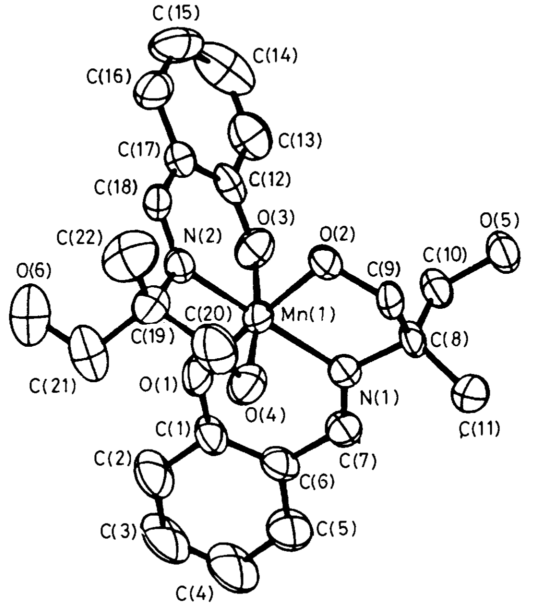

Figure 1. An ORTEP projection of Mn(saladhp)$_2$. Ellipsoids are at 50% probability. Important distances (Å) and angles (°): Mn(1)–O(1), 1.903(6); Mn(1)–O(2), 1.854(6); Mn(1)–O(3), 1.909(7); Mn(1)–O(4), 1.923(7); Mn(1)–N(1), 1.997(7); Mn(1)–N(2), 2.013(7). O(1)–Mn(1)–O(2), 173.5(3); O(1)–Mn(1)–O(3), 86.8(3); O(1)–Mn(1)–O(4), 89.1(3); O(1)–Mn(1)–N(1), 90.9(3); O(1)–Mn(1)–N(2), 96.6(3); O(2)–Mn(1)–O(3), 90.8(3); O(2)–Mn(1)–O(4), 94.0(3); O(2)–Mn(1)–N(1), 83.4(3); O(2)–Mn(1)–N(2), 89.5(3); O(3)–Mn(1)–O(4), 171.6(3); O(3)–Mn(1)–N(1), 98.7(3); O(3)–Mn(1)–N(2), 90.2(3); O(4)–Mn(1)–N(1), 88.6(3); O(4)–Mn(1)–N(2), 82.9(3); N(1)–Mn(1)–N(2), 168.6(3).

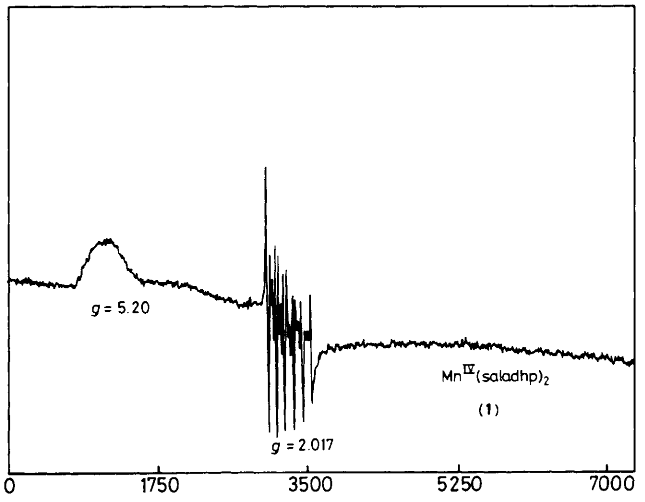

Figure 2. E.s.r. spectrum of Mn(saladhp)$_2$ in DMF–MeOH (1 : 1) at 100 K. Microwave frequency, 9.29 GHz; power, 20 mW; time constant, 50 s; gain 25 × 10^5, Mn nuclear hyperfine coupling constant is 89 G.

plantarum.[3] Both enzymes may have a catalytically accessible Mn^{IV} intermediate.

For this reason, we are attempting to define the physical properties and reactivity of Mn^{IV} complexes to a more sophisticated level of chemical resolution. Our approach is to synthesize and characterize Mn^{IV} complexes containing nitrogen and oxygen ligands which mimic functional groups native to biological systems. In this communication we report the structural and spectroscopic characterization of a mononuclear Mn^{IV} Schiff base complex which may be relevant to the understanding of the manganese centres in biological systems.

All manipulations were carried out using standard inert atmosphere techniques and distilled solvents. Mn^{IV}(saladhp)$_2$ (**1**) was synthesized by the reaction of salicylaldehyde and 1,3-dihydroxy-2-amino-2-methylpropane (1 : 1 ratio) in dimethylformamide (DMF) under reflux for 1.5 h. After cooling to room temperature, 0.5 equiv. of Mn^{III} acetate and 2.5 equiv. of NaOH dissolved in degassed DMF were added and the reaction refluxed for an additional 10 h. The mixture was then exposed to air, generating a deep red solution. Crystals suitable for *X*-ray diffraction studies were obtained from DMF–diethyl ether (1 : 1) by standing overnight at 4 °C.‡

The structure of Mn(saladhp)$_2$ is illustrated in Figure 1. The saladhp ligand is tridentate and forms a meridional bis chelate with one phenolate oxygen, one deprotonated hydroxy oxygen, and one imine nitrogen atom co-ordinated to the metal. An additional hydroxy group of each ligand remains unco-ordinated. The Mn^{IV} ion in the complex shows a slightly distorted octahedral geometry with the majority of angles about Mn^{IV} being nearly 90° or 180° (Figure 1); however, some strain is associated with co-ordination of the alkoxy oxygen atoms [*e.g.*, O(2)–Mn(1)–N(1), 83.4(3) and O(4)–Mn(1)–N(2), 82.9(3)°]. The Mn^{IV}–O [1.854(5)—1.923(7) Å] and Mn^{IV}–N [1.997(7) and 2.013(7) Å] bond lengths are similar to those recently reported[6] for Mn^{IV}(sal)$_2$(bipy) (H$_2$sal = salicylic acid; bipy = 2,2′-bipyridine) Mn^{IV}–N [2.041(6)—2.052(6) Å] and Mn^{IV}–O [1.823(5)—1.889(5) Å]. In both cases, the basic co-ordination geometry is as expected for a d^3 ion.

The formulation of (**1**) as an Mn^{IV} complex is supported by the room temperature solid state magnetic moment (3.91 μ_B). The e.s.r. spectrum of (**1**) in DMF–MeOH (Figure 2)§ is also consistent with a spin 3/2 ion. The six line hyperfine (a = 89 G) arising from ^{55}Mn(I = 5/2), and nitrogen superhyperfine structure is evident in the component at g = 2. An additional signal, which is temperature dependent, is observed at lower field. The appearance of an e.s.r. spectrum for a d^3 sytem will depend on the zero field splitting parameters.[7] When the axial parameter D is small (*i.e.* $2D \ll h\nu$ where $h\nu = 0.31\ \mathrm{cm}^{-1}$ at 9.3 GHz) the feature at g = 2 is the predominant signal. This pattern is observed for (**1**) (Figure 2), tris(thiohydroxamato)-[7c] and tris(dithiocarbamato)-Mn^{IV}.[8] In contrast, Mn^{IV} catecholate[9] and sorbitol[10] complexes have a dominant low

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‡ *Crystal data* for (**1**): C$_{28}$H$_{40}$MnN$_4$O$_8$, monoclinic, space group $P2_1/a$, Z = 4, a = 10.676(5), b = 16.473(10), c = 17.541(7) Å, β = 102.82(4)°, U = 3008(3) Å^3, T = 25 °C, crystal dimensions 0.090 × 0.310 × 0.520 mm; data were collected $0 \leqslant 2\theta \leqslant 45°$ on a Syntex P2$_1$ four circle diffractometer. The data were reduced using the SHELX[4] program package; structure was solved using the direct methods program MULTAN78;[4] least squares refinement used the SHELX program package. Complex atomic scattering factors were used in refinement.[5] Non-hydrogen atoms of Mn(saladhp)$_2$ were refined with anisotropic thermal parameters. Solvent molecules were refined using isotropic thermal parameters. Hydrogen atoms were included at calculated positions with fixed U values (isotropic thermal parameters) of 0.05 Å^2. 4657 Data were collected with 2186 data > 3σ(I); D_C = 1.359, D_m = 1.35 by flotation (hexane–CCl$_4$). The structure refined with R = 0.076 and R_2 = 0.072. The largest non-solvent residual was 0.34 e/Å^3. 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, 1986.

§ 1 G = 10^{-4} T.

field resonance indicating that D is large in these systems. This is a somewhat surprising observation as one might expect (**1**) to resemble electronically the catecholate and sorbitol complexes more closely than the thiohydroxamate or dithiocarbamate compounds.

The u.v.–visible spectrum of (**1**) shows a strong u.v. absorbance with shoulders at 401 nm (ε 6 908 dm^3 mol^{-1} cm^{-1}), 479 (3 314), and 562 (1 724). Cyclic voltammetry of (**1**) using a platinum electrode in dimethyl sulphoxide solution (DMSO) containing 0.1 M tetrabutylammonium hexafluorophosphate displayed a quasi-reversible one-electron reduction with $E_{pc} = -0.460$ V (*vs.* Ag/AgCl).¶ This potential compares with +0.44 V (in DMF, *vs.* standard calomel electrode) determined for Mn^{IV}(sal)$_2$(bipy). Thus, the Mn^{IV} ion in (**1**) is stabilized by nearly 1 V‖ with respect to Mn^{IV}(sal)$_2$(bipy). This observation reflects the ability of the alkoxide functional group, which is a strong Lewis base, to stabilize high oxidation states. (**1**) is indefinitely stable in air as a solid or in solution. Whereas other Mn^{IV} compounds are moisture sensitive,[11] (**1**) is soluble and very stable in water. In fact, we have been unable to generate O_2 photochemically using (**1**) even under the conditions reported by McAuliffe[12] which leads to the photo-oxidation of water by Mn^{III} Schiff base complexes.

The data reported herein will help establish a literature for the physical properties and chemical reactivity of Mn^{IV} complexes. This report documents the first structurally characterized Mn^{IV} Schiff base complex and also is the first structural presentation of a Mn^{IV} alkoxide complex. The electrochemical behaviour of (**1**) demonstrates that the redox potential for Mn^{IV} in an N_2O_4 co-ordination environment can span nearly 900 mV.

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¶ $\Delta E_p \cong 100$ mV, $i_{pa}/i_{pc} = 0.75$, scan rate 150 mV/s, concentration $I \approx 10^{-3}$ M. In aqueous solution, the electrochemical trace is complex and irreversible with $E_p \cong -437$ mV *vs.* Ag/AgCl, scan rate 150 mV/s.

‖ The Ag/AgCl reference electrode is about 45 mV more negative than standard calomel electrode (S.C.E.). Therefore, $E_{pc} \approx -0.5$ V *vs.* S.C.E. for (**1**). The E_{pc} for (**1**) is identical in DMF.