A Manganese(IV) Complex with Phenoxide- and Carboxylate-like Ligation: Preparation and Structure of [Mn(sal)$_2$(bipy)] (H_2sal = Salicylic Acid; bipy = 2,2′-Bipyridine)

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Neutral [Mn(sal)$_2$(bipy)] (**1**) (H_2sal = salicylic acid; bipy = 2,2′-bipyridine) has been obtained as one of the products from the reaction of $[Mn_2O_2(bipy)_4]^{3+}$ (**2**) with NaHsal, and contains a distorted octahedral Mn^{IV}–O_4N_2 co-ordination unit of potential importance to high oxidation state manganese biomolecules.

Biological water oxidation during photosynthesis leads to the evolution of molecular dioxygen and a supply of electrons for photosystem II (PSII) of the photosynthetic apparatus (equation 1).[1] The involvement of manganese atoms in this reaction is well established, and it is widely suspected that they represent the site of binding and oxidation of the water molecules.[2] Studies aimed at elucidating the structure of the manganese site at a molecular level have shown, among other things, the absence of porphyrin rings, an inner co-ordination sphere comprising O and/or N atoms, and redox cycles encompassing high metal oxidation states (II, III, and/or IV).[1—6] As part of our programme directed towards the synthesis of a satisfactory inorganic model for this site we have been developing the co-ordination chemistry of high oxidation state manganese with the type of ligand functions likely to be binding the metal in the natural system; this is a poorly investigated area at present. One ligand finding much utility with us is salicylic acid (*o*-hydroxybenzoic acid, H_2sal), whose phenoxide and carboxylate functions are being used as convenient substitutes for the amino acid side groups of tyrosine and aspartic/glutamic acid, respectively. We herein report the preparation and structure of a manganese(IV) monomer containing this ligand. All operations were performed exposed to the atmosphere using solvents as received.

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

Treatment of mixed-valence $[Mn_2O_2(bipy)_4](ClO_4)_3$ $2H_2O$[7] (**2**) (bipy = 2,2′-bipyridine) with NaHsal (4 equiv.) in MeCN solution led to the fairly rapid precipitation of a brown microcrystalline material. After *ca.* 15 min, the mixture was filtered and the essentially black mother liquor placed in a freezer (−20 °C). After overnight storage, large black prisms of (**1**) were collected by filtration. Recrystallization from dimethylformamide (DMF)–MeCN gave (**1**) as the MeCN solvate in 31% yield based on available Mn^{IV}.†

[Mn(sal)$_2$(bipy)] (**1**) $[Mn_2O_2(bipy)_4](ClO_4)_3 \cdot 2H_2O$ (**2**)

The structure of (**1**) is shown in Figure 1. The manganese(IV) atom is six-co-ordinate and possesses an N_2O_4 ligand environment. Complex (**1**) has no crystallographically imposed symmetry, but does approach C_2 symmetry, with the rotation axis passing through Mn and the mid-point of the N(2) · · · N(13) vector. The phenoxide oxygen atoms O(23) and O(33) are *cis*, and the carboxylate oxygen atoms O(14) and O(24) are *trans* about the Mn. With the exception of the internal bipy angle N(2)–Mn–N(13) [78.89(25)°], which is restricted by the five-membered chelate ring, angles at Mn are reasonably close to 90 or 180°, being in the range 86.67(23)—95.46(24) and 171.56(25)—172.88(23)°, respectively. The Mn^{IV}–N bond lengths [2.041(6) and 2.052(6) Å] are similar to those in the trapped-valence parent compound (**2**) (2.016—2.075 Å)[7a] and those to the *trans* pyridine ligands of Mn(dtb)$_2$(pyr)$_2$ (dtb = 3,5-di-t-butylcatecholate; pyr = pyridine) [2.018(3) Å].[8] The Mn^{III}–N lengths of (**2**) are significantly longer as expected (2.134—2.226 Å). Similarly, the Mn–phenoxide and –carboxylate bond lengths are noticeably shorter than corresponding linkages in Mn^{III} species.[9]

The magnetic moment of (**1**) was measured in dimethyl sulphoxide (DMSO) solution using the Evans n.m.r. method.[10] The value obtained (3.83 μ_B) is fully consistent with a d^3 Mn^{IV} centre. Cyclic voltammetric studies at a glassy carbon electrode in DMF containing 0.1 M tetra-n-butylammonium perchlorate displayed an irreversible reduction at +0.44 V *vs.* standard calomel electrode. The electronic spectrum of (**1**) in DMF displayed bands with maxima at 575 (ε_M = 2650 l mol^{-1} cm^{-1}) and 295 nm (26 650), and a shoulder at *ca.* 340 nm (10 600). Complex (**1**) seems indefinitely stable in air in the solid state and reasonably stable in solution. In DMF or DMSO, only after several hours at room temperature is significant change observed, the initial black colour of (**1**) slowly yielding a dark green solution.

The preparation of (**1**) from (**2**) represents a convenient synthetic route, for (**2**) is readily available in high yield using a straightforward procedure.[7b] The Mn^{IV} atom in (**2**) is initially bound to two bipy groups and two bridging oxide atoms. Formation of (**1**) thus entails substituting two sal^{2-} groups for one of the bipy ligands and both of the oxides. A better understanding of the course of the reaction must, however, await identification of the other major product, the initial brown microcrystalline precipitate. This material is soluble in DMF to give a deep red solution and is not, therefore, a decomposition product, *e.g.*, a manganese oxide.

Complex (**1**) joins only a handful of structurally characterized Mn^{IV} species, most of which are monomeric and contain catecholate[8,11,12] or porphyrin[13,17] ligation, neither of which have been detected as binding to manganese in biological systems. The structures of $MnCl_6^{2-}$,[14] MnF_6^{2-},[15] and $MnMe_4$(dmpe)[16] [dmpe = 1,2-bis(dimethylphosphino)-

† *Crystal data:* $C_{28}H_{22}MnN_4O_6$, M_r = 565.45, triclinic, space group $P\bar{1}$, Z = 2, a = 18.066(9), b = 9.410(3), c = 8.356(3) Å, α = 85.87(2), β = 107.23(2), γ = 112.08(2)°, U = 1256.07 Å^3, t = −157 °C, crystal dimensions 0.21 × 0.22 × 0.30 mm; data were collected in the range 6 ≤ 2θ ≤ 45°. The structure was solved by a combination of direct methods and Fourier techniques, and refined by full-matrix least squares. All non-hydrogen atoms were refined with anisotropic thermal parameters, except the solvent molecules which were refined isotropically. In the latter stages, hydrogen atoms were included in calculated positions with isotropic thermal parameters. 2411 unique reflections with $F > 2.33\sigma(F)$ were refined to conventional values of R = 7.42% and R_w = 6.98%. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

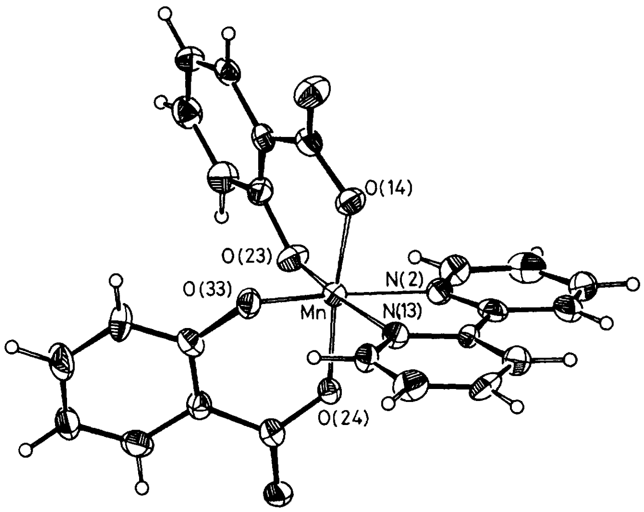

Figure 1. An ORTEP projection of (**1**). Non-hydrogen atoms are depicted as 50% probability ellipsoids, hydrogen atoms as spheres of arbitrary size. Pertinent distances (Å) and angles (°): Mn–N(2), 2.052(6); Mn–N(13), 2.041(6); Mn–O(14), 1.862(5); Mn–O(23), 1.823(5); Mn–O(24), 1.889(5); Mn–O(33), 1.835(5); O(14)–Mn–O(23), 93.93(23); O(14)–Mn–O(33), 90.31(23); O(23)–Mn–O(33), 95.46(24); O(24)–Mn–O(33), 93.03(22); O(24)–Mn–O(23), 92.01(22); N(2)–Mn–O(14), 88.97(14); N(13)–Mn–O(33), 92.94(24).

ethane] are also known, as are those of di-[17] and tetranuclear[18] species.

The attainment of (**1**) represents an important step forward in our development of high oxidation state manganese chemistry with ligand types that may be occurring at the water oxidation site, for it establishes that Mn^{IV} can be obtained with phenoxide- and carboxylate-like ligation. In addition, (**1**) should prove useful in e.s.r. and EXAFS studies for comparison of obtained parameters with those being accumulated on the native site.[1–6]

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