Isolation of a Remarkably Stable Hydrogen Bonded Dimeric Manganese(II) Complex, $[Mn(L)(OH_2)]_2(Me_2SO)_2$ from the Reduction of a Manganese(III) Schiff Base Complex [L = the Dianion of *N,N'*-Bis(3-bromo-5-nitrosalicylidene)-1,2-diamino-(2-methyl)ethane]

Manuel R. Bermejo,*[a] **Ana Garcia-Deibe,**[a] **Jesus Sanmartin**[a] **and Antonio Sousa,***[a] **Nadeem Aurangzeb,**[b] **Charlotte E. Hulme,**[b] **Charles A. McAuliffe,***[b] **Robin G. Pritchard**[b] **and Michael Watkinson**[b]

[a] *Departmento de Quimica Inorganica, Universidad de Santiago, E-15706 Santiago de Compostela, Spain*
[b] *Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester, UK M60 1QD*

The crystal structure of $[Mn(L)(OH_2)]_2(Me_2SO)_2$ [L = the dianion of *N,N'*-bis(3-bromo-5-nitrosalicylidene)-1,2-diamino-(2-methyl)ethane] shows it to be a strongly hydrogen-bonded dimer of manganese(II), produced by recrystallisation of a manganese(III) Schiff base acetate complex from dimethyl sulfoxide.

The chemistry of manganese is the subject of much current interest owing to its involvement in a number of biological systems *e.g.* in superoxide dismutase[1] and an azide insensitive catalase.[2] The role of manganese in the oxygen-evolving complex (OEC) of photosystem II (PSII) is of great importance.[3,4] The necessity for a manganese complex to catalyse the decomposition of water is highlighted by manganese depletion studies carried out on spinach leaf chloroplasts.[5] These showed that no other metal could reactivate lost O_2-evolving activity when all the manganese had been extracted from the chloroplasts.

It is well established that four manganese ions are necessary for high rates of oxygen evolution.[3] EXAFS studies,[6] and further XANES studies[7] have revealed that these four ions are arranged in two inequivalent binuclear environments with two distinct Mn···Mn separations. The first is a short distance of *ca.* 2.7 Å bridged by a μ_2-oxo system and the second is a longer separation of *ca.* 3.3 Å, which may be bridged by a carboxylate group. As a consequence of this, model complexes have been synthesised based on these structural motifs.[8] However, to date, dioxygen has only been generated from a model dinuclear manganese system.[9] We have continued to use similar tetradentate N_2O_2 Schiff base ligands, with a view to coordinate water to complete the octahedral geometry around the manganese ions, and more effectively mimic the OEC.

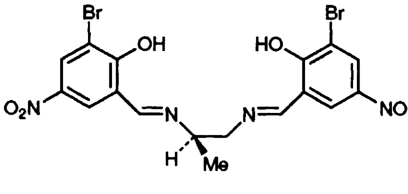

Fig. 1

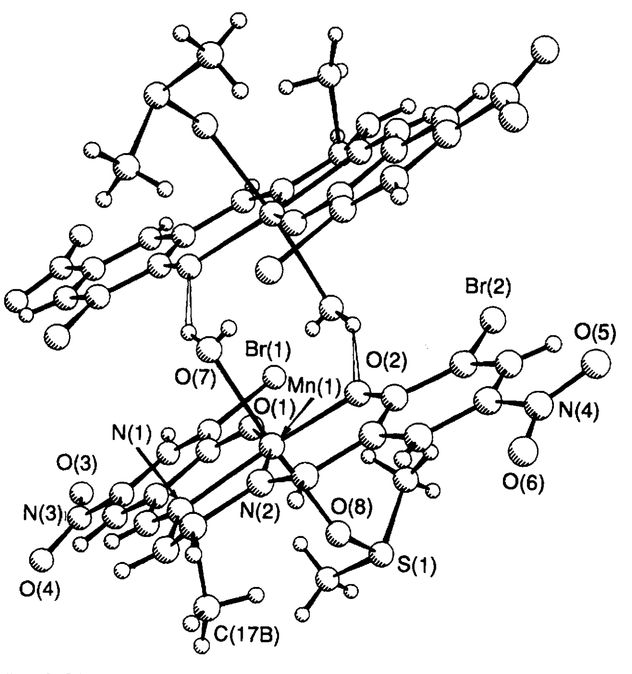

Fig. 2 The crystal structure of $[Mn(L)(H_2O)]_2(Me_2SO)_2$. Selected bond lengths: Mn(1)–O(1) 2.086(5), Mn(1)–O(2) 2.081(6), Mn(1)–N(1) 2.170(8), Mn(1)–N(2) 2.163(7), Mn(1)–O(7) 2.269(9), Mn(1)–O(8) 2.219(7) Å.

Recently,[10] we reported the synthesis and crystallographic characterisation of the polymeric manganese(III) Schiff base complex $[Mn(salpn)(OAc)]_{2n}(H_2O)_{3n}$ [salpn = the dianion of *N,N'*-bis(salicylidene)-1,3-diaminopropane] from the reaction of manganese(II) acetate and H_2salpn. Subsequently, we have extended our investigation to the use of manganese(III) acetate with tetradentate Schiff bases. Our findings show that similar manganese(III) complexes can be isolated based on elemental analyses, IR spectroscopy, FAB MS and magnetic susceptibility measurements.[11] In an attempt to recrystallise the complex $[Mn(L)(OAc)(OH_2)_2]$ from a dimethyl sulfoxide solution, however, the title compound was isolated and crystallographically characterised.†

Examples of manganese(II) complexes employing nitrogen- and oxygen-based ligands have been crystallographically characterised, but these generally utilize macrocyclic ligands,[14] or ligands based on 2,6-diacetylpyridine[15] to stabilize the manganese(II) ion. There are a few examples of air stable manganese(II) complexes with Schiff base ligands of N_2O_2-coordination[16] but none, to our knowledge, with a ligand containing an asymmetric carbon backbone. The asymmetric carbon atoms in L produces a 70%–30% racemic mixture in the crystal system. The structure of $[Mn(L)(OH_2)]_2(Me_2SO)_2$ consists of an N_2O_2 coordination sphere around each manganese(II) atom with capping water and dimethyl sulfoxide groups in the axial positions. The closeness of the water molecules between the manganese(II) moieties leads to the very strong hydrogen bonding and consequently the short Mn···Mn separation of 4.6 Å. The dimerisation is also facilitated by the strong π-interaction between overlapping ligand orbitals, which leads to the high degree of symmetry observed in the structure.

We have previously reported the isolation of the manganese(IV) complex $[Mn(salpn)O]_2(Me_2SO)_2$[17] from the facile aerial oxidation of a manganese(III) complex in a dimethyl sulfoxide solution, which makes the isolation of the title compound from the reduction of a manganese(III) complex quite remarkable. The inherent stability of manganese(III) Schiff base complexes would be expected to render them incapable of reduction to the less stable manganese(II) species, especially under aerobic conditions. It may be that the oxidising nature of manganese(III) in this case acts to oxidise dimethyl sulfoxide to dimethyl sulfone accompanied by the concurrent reduction of manganese(III) to manganese(II). The appearance of a peak attributable to dimethyl sulfone in the

GC–MS trace shows an increase in the level compared to the background reading, which can partially substantiate this process.

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Footnote

† *Crystal data* for $C_{19}H_{19}N_4SO_8Br_2Mn$: M = 678.19, triclinic space group $P\bar{1}$, a = 11.649(6), b = 12.551(7), c = 9.280(5) Å, α = 91.84(4), β = 97.40(4), γ = 112.44(3)°, V = 1239(2) Å^3, D_c = 1.818 g cm^{-3}, Z = 2. Graphite monochromated Mo–Kα radiation (λ = 0.71069 Å) employing a Rigaku A5C6s diffractometer. 4588 Reflections were collected using ω–2θ scans, 4356 of which were unique; 2019 were considered observed [$I > 3\sigma(I)$]. The structure was solved by direct methods (MITHRIL),[12] and refined by full-matrix least-squares techniques (TEXSAN).[13] This gave final residual factors of R = 0.042 and R_w = 0.044. The methyl groups attached to the carbon backbone were disordered over two sites [C(17A) 70%, C(17B) 30%]. All non-hydrogen atoms were treated anisotropically and the hydrogen atoms isotropically, except those attached to the methyl carbon atoms which were constrained to chemically reasonable positions (C–H = 0.95 Å). 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.

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