Towards Functional Models of the Photosynthetic Water Oxidation Centre: Synthesis and Structure of the Asymmetric Complex $[Mn_2O(O_2CMe)_2(bpy)_2(H_2O)(S_2O_8)]\cdot H_2O$ (bpy = 2,2′-bipyridine), containing Coordinated H_2O and $S_2O_8{}^{2-}$

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The asymmetric complex $[Mn_2O(O_2CMe)_2(bpy)_2(H_2O)(S_2O_8)]\cdot H_2O$ **1** has been prepared in good yield from oxidation of $Mn(O_2CMe)_2\cdot 4H_2O$ by $S_2O_8{}^{2-}$ in aqueous solution and has been characterized by elemental analysis, IR spectroscopy and X-ray crystallography; the complex possesses both terminally ligated H_2O and $S_2O_8{}^{2-}$ groups, the latter with an exceptionally long O–O bond.

We are currently involved in the development of synthetic methodologies for the preparation of high oxidation state (Mn^{III} and Mn^{IV}) polynuclear Mn complexes as models for Mn-containing biomolecules such as Mn-catalase[1] and the water oxidation centre (WOC) of photosystem II.[2] Previous work in this laboratory has focused on the comproportionation of Mn^{II} and Mn^{VII} in nonaqueous media as one method of choice for the preparation of high nuclearity (n = 2–12) Mn^{III} and Mn^{IV} clusters.[3] We have now extended our efforts to other reagents capable of oxidizing Mn^{II} to Mn^{III} and beyond, and are also investigating reactions in aqueous solution in the hope of obtaining H_2O-bound species for water oxidation studies.

The peroxydisulphate ion, $S_2O_8{}^{2-}$, is one of the strongest oxidants known (E° = 2.01 V) and is thermodynamically capable of oxidizing Mn^{II} to Mn^{VII}. It was used by Nyholm and Turco as the oxidant in their original synthesis of the $Mn^{III,IV}$ oxo-bridged dimer $[Mn_2O_2(bpy)_4]^{3+}$ in aqueous solution.[4] It has also been used previously to oxidize $[Mn_2O(O_2CMe)_2L_2]^{2+}$ to the trication,[5a] and to access high oxidation

Table 1 Comparative metrical data for manganese complexes

Complex	d(Mn···Mn)/Å	d(Mn–O$_{bridge}$)/Å	∠(Mn–O–Mn)/°
$[Mn_2O(O_2CMe)_2(bpy)_2(S_2O_8)(H_2O)]^a$	3.145(5)	1.735(10); 1.810(10)	125.1(6)
$[Mn_2O(O_2CMe)_2(bpy)_2(H_2O)_2]^{2+b}$	3.132	1.781(5); 1.784(5)	122.9
$[Mn_2O(O_2CMe)_2\{HB(pz)_3\}_2]^c$	3.175(1)	1.790(3)^g	125.0(3)
$[Mn_2O(O_2CMe)_2\{HB(pz)_3\}_2]^d$	3.159(1)	1.773(2); 1.787(2)	125.1(1)
$[Mn_2O(O_2CMe)_2(tacn)_2]^{2+e}$	3.084(3)	1.80(1)^g	117.9(2)
$[Mn_2O(O_2CMe)_2(bpy)_2Cl_2]^f$	3.153(3)	1.777(12); 1.788(11)	124.3(7)

[a] This work. [b] Ref. 7, MeCN. [c] Ref. 12; pz = pyrazolyl. [d] Ref. 12, 4 MeCN. [e] Ref. 13; tacn = 1,4,7-triazacyclononane. [f] Ref. 14. [g] Molecule lies on a two-fold rotation axis.

states of other transition metals (Ag^{2+},[5b,c] Ni^{3+} [5d]) in aqueous solution. Despite the fact that it should be a relatively good O-donor, there appears to be only one crystallographically characterized example of $S_2O_8^{2-}$ coordinated to a transition metal ion.[6] We herein report the preparation and characterization of $[Mn_2O(O_2CMe)_2(bpy)_2(H_2O)(S_2O_8)]$ **1** *via* oxidation of $Mn(O_2CMe)_2{\cdot}4H_2O$ with $(NH_4)_2S_2O_8$ in aqueous solution, including the observation of an Mn-bound $S_2O_8^{2-}$ group with a remarkably long O–O bond.

To a yellow solution of $Mn(O_2CMe)_2{\cdot}4H_2O$ (2.00 g, 8.16 mmol) and 2,2′-bipyridine (1.27 g, 8.13 mmol) in H_2O–HO_2CMe (20 ml–6 ml) was added $(NH_4)_2S_2O_8$ (1.86 g, 8.15 mmol). The resulting solution, which slowly turned dark brown, was filtered and left at room temperature overnight. The resulting black crystals of **1** were collected by filtration, washed with ice-cold water (2 × 3 ml) and ethanol (2 × 3 ml), and dried in air. The yield was 50–55% based on Mn. Satisfactory analytical data (C, H, N, S, Mn) were obtained.

The structure† of **1** (Fig. 1) consists of a dinuclear Mn unit bridged by one oxide and two μ-acetate-*O,O′* ligands. One bpy ligand is coordinated to each Mn and ligation at each metal centre is completed by a water molecule [Mn(1)] or a peroxydisulphate anion [Mn(2)]. Charge considerations and observation of Jahn–Teller elongation of the Mn(1)–O(5), Mn(1)–O(7), Mn(2)–O(9) and Mn(2)–O(10) bonds show the metals to be at the Mn^{III} oxidation level. Two bond lengths within **1** are especially worthy of note. The Mn(1)–O(5) distance of 2.176 Å is significantly shorter than the corresponding Mn^{III}–OH_2 distances in $[Mn_2O(O_2CMe)_2(bpy)_2(H_2O)_2]^{2+}$ **2**[7] [2.293(6) and 2.331(6) Å], but is comparable to those found in $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]{\cdot}2MeCO_2H{\cdot}4H_2O$ **3**[8] and $[Mn_4O_2(O_2CPh)_9(H_2O)]^-$ **4**[9] [2.18(1) and 2.102(13) Å, respectively]. In both of the latter molecules the terminal H_2O ligands are engaged in extensive inter- and intra-molecular hydrogen bonding. Similarly, complex **1** contains a hydrogen bond between the coordinated H_2O molecule and the water of crystallization [O(5)···O(48) = 2.51 Å]. No such interaction occurs in **2**. The O(14)–O(15) distance within the $S_2O_8^{2-}$ ligand is very much longer [1.604(20) Å] than those found in $Cu(bpy)_2(S_2O_8)$ (1.467 Å),[6] $S_2O_8^{2-}$ (1.31 Å)[10] and H_2O_2 (1.453 Å).[11] Complex **1** is the first example of an asymmetric Mn_2^{III} complex containing the (μ-O)(μ-O_2CMe)$_2$ core. Other Mn_2^{III} complexes containing this core[7,12–14] have been advanced as possible models for

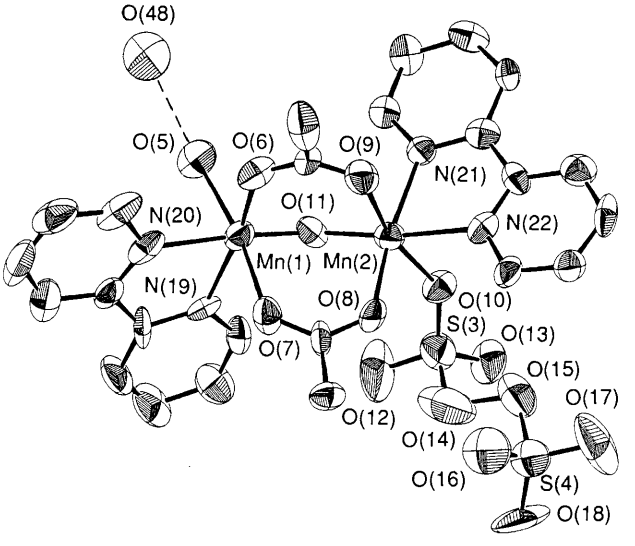

Fig. 1 Structure of complex **1** showing the atom labelling scheme. Selected bond distances (Å) and angles (deg.): Mn(1)–O(11) 1.735(10), Mn(1)–O(5) 2.176(12), Mn(1)–O(6) 1.949(12), Mn(1)–O(7) 2.147(11), Mn(1)–N(19) 2.100(13), Mn(1)–N(20) 2.070(14), Mn(2)–O(11) 1.810(10), Mn(2)–O(8) 1.933(11), Mn(2)–O(9) 2.152(12), Mn(2)–O(10) 2.231(11), Mn(2)–N(21) 2.057(12), Mn(2)–N(22) 2.090(13), O(14)–O(15) 1.604(20) O(5)···O(48), 2.51, Mn(1)–O(11)–Mn(2) 125.1(6).

Mn-catalase, which is thought also to possess an $[Mn_2O(O_2CR)_2]^{2+}$ bridging unit.[15] Comparative data for these complexes are given in Table 1. It can be seen that, in keeping with the overall asymmetry of **1**, the bridging oxide ligand is located markedly closer to Mn(1), presumably as a result of the dianionic nature of the $S_2O_8^{2-}$ ligand on Mn(2).

Preparation of **1** utilised one equivalent of $S_2O_8^{2-}$ per Mn, which could have converted all initial Mn^{II} to Mn^{IV}. It may be that because the oxidation is slow, complex **1** crystallises prior to its further oxidation. Treatment of the yellow $Mn(OAc)_2{\cdot}4H_2O$–bpy reaction mixture with 0.5 equivalents of $(NH_4)_2S_2O_8$ gives a different, as yet uncharacterized, black crystalline product whose IR spectrum now shows SO_4^{2-}, rather than peroxydisulphate bands. This is currently believed to be a similar Mn_2^{III} species but possibly containing coordinated SO_4^{2-} instead of $S_2O_8^{2-}$.

Preliminary experiments utilizing other carboxylates and chelates in the $S_2O_8^{2-}$ oxidations show the reaction not to be limited solely to the formation of Mn_2^{III} species. Use of propionic acid (HO_2CEt) and $Mn(O_2CEt)_2{\cdot}4H_2O$ instead leads to formation of the propionate 'butterfly' complex $[Mn_4O_2(O_2CEt)_7(bpy)_2]^+$,[16] while $Mn(OAc)_2{\cdot}4H_2O$ and picolinic acid (Hpic) give the Mn_2^{IV} dimer $Mn_2O_2(pic)_4$.[17] Oxidation of Mn^{2+} by $S_2O_8^{2-}$ in aqueous solution thus represents an easy and efficient method for the preparation of high oxidation state polynuclear Mn complexes, avoiding the

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† *Crystal data* for **1**: $C_{24}H_{26}N_4O_{15}Mn_2S_2$, monoclinic, $P2_1/c$, a = 7.918(2), b = 21.840(6), c = 17.354(5) Å, β = 91.93(1)°, V = 2999.30 Å^3, Z = 4, R = 0.0922, R_w = 0.0821 for 1998 reflections with $F > 2.33\sigma(F)$. Mo-Kα radiation, T = −169 °C. The structure was solved by a combination of direct methods (MULTAN 78) and Fourier techniques. The Mn and S atoms' positions were obtained from an initial E-map and the remaining non-hydrogen atoms were found in subsequent iterations. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms (except water molecules) were introduced in fixed, calculated positions. 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.

decomposition and disproportionation reactions that have historically been associated with the aqueous chemistry of higher oxidation state Mn.

In addition to the purely 'inorganic' interest in an $S_2O_8^{2-}$ ligand, complex **1** also augurs well for our water oxidation efforts. The binding of both H_2O *and* a strong oxidizing agent to the same Mn complex provides the components for a Mn-catalysed conversion of $2H_2O$ to O_2. It is of potential relevance to note that the $S_2O_8^{2-}$ has been activated (O–O bond lengthened) by binding to Mn and that the bound H_2O is hydrogen-bonded to another H_2O molecule. Systematic screening of a variety of reaction conditions is in progress in an attempt to effect O_2 release from this and related systems.

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