Synthesis of a Bis-Manganese Water Splitting Complex

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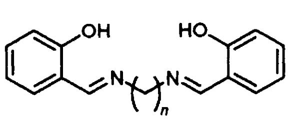
Complex **8** has been prepared by an efficient one-step manganese-templated condensation/macrocyclisation; upon irradiation using visible light in water in the presence of *p*-benzoquinone, complex **8** demonstrates the ability to split water.

The most important role of manganese in nature identified to date is its involvement at the Oxygen Evolution Centre (OEC) of Photosystem II (PSII) within the photosynthetic apparatus of green plants and cyanobacteria.[1] Direct biochemical and biophysical studies of the chloroplast-associated OEC have provided significant insight into the mechanism and structure of the enzyme complex responsible for the water splitting reaction.[1b,c,2] Amongst the important conclusions from this work are that: (*i*) four manganese ions are required for the reaction, although it is possible that two of these are only structural factors; (*ii*) some or all of the manganese ions are associated in clusters, coordinated by oxygen and nitrogen donor atoms; (*iii*) there are two Mn···Mn separations of *ca.* 2.7 and 3.3 Å.



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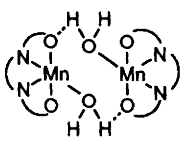

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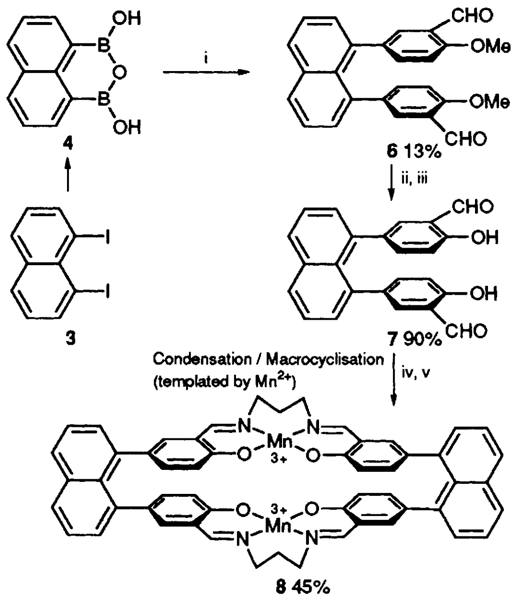

Scheme 1 *Reagents and conditions*: i, 5-bromo-2-methoxybenzaldehyde **5**, 2% $Pd(Ph_3)_4$, Na_2CO_3, DMF, H_2O, heat, 19 h; ii, BBr_3, CH_2Cl_2; iii, H_2O; iv, K_2CO_3, $Mn(ClO_4)_2{\cdot}H_2O$; v, 1,3-diaminopropane

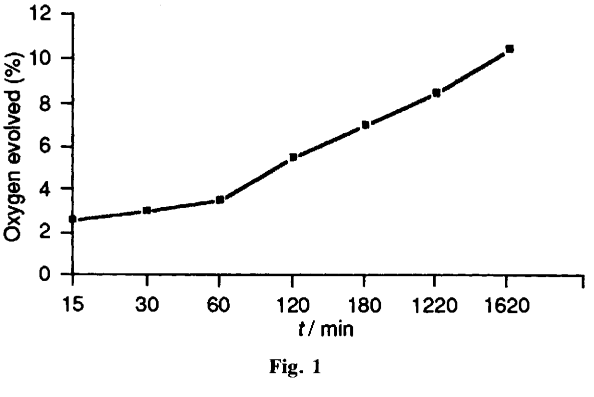

Fig. 1

We have pursued binuclear manganese complexes of N_2O_2 donor set tetradentate Schiff bases **1** and have achieved the only success reported to date of splitting water with a model manganese complex **2**, which evolves dioxygen upon photolysis, along with the simultaneous reduction of *para*-benzoquinone to hydroquinone.[3] Previous work has shown that this N_2O_2 donor set of the tetradentate ligands **1** provide the necessary coordination sphere for manganese(III) to allow light-driven water photolysis, provided that the ligand backbone between the imine groups is either dimethylene, trimethylene or tetramethylene, although activity is far superior for the trimethylene [**1** (n = 3)] backbone; it may be concluded that the N_2O_2 donor set linked by the trimethylene bridge mimics natural PSII. Here, we report the synthesis of the first bis-manganese complex **8** in which the two metal centres are held proximal by a single macrocyclic ligand, which is also active as a water splitting complex.

The unoptimised synthesis of complex **8** is shown in Scheme 1, which employed the reaction of boronate **4** (readily available from 1,8-diidonaphthalene in 60% yield[4]) with commercially available bromide **5** under palladium(0) catalysed cross-coupling conditions,[5] which afforded dialdehyde **6** in an unoptimised yield of 13%.† After removal of the methyl ether of **6** with boron tribromide to afford phenol **7**,‡ we then used a highly efficient manganese(II) template assisted construction of the macrocyclic ligand using 1,3-diaminopropane on the manganese complexed phenol **7**, to give the oxidised manganese(III) complex **8** in one step as the perchlorate salt. The successful synthesis of complex **8** (containing coordinated water) is evidenced by the following: IR stretches at 3000–3400 br (OH, typical of water coordinated to Mn), 1620s (coordinated C=N), and 1080 br (uncoordinated ClO_4^+); *m*/*z* (FAB) 919 (M + H^+); no peak is observed relating to the complex $[Mn_2L](ClO_4)_2$ presumably due to the poor coordination properties of the perchlorate counterion.§

Most importantly, when complex **8** (insoluble in water) was suspended in water in the presence of *p*-benzoquinone at 25 °C and irradiated with a 300 W tungsten lamp over an 18 h period, oxygen evolution was detected,¶ as shown in Fig. 1. Although complex **8** showed activity as a water splitting complex, it was not as active as unconstrained complexes previously reported.[3] However, it is important to note that **8** is the first example of a custom-designed water splitting bis-manganese complex, in which the two metal atoms are held in proximity by a single macrocyclic ligand. Further developments are underway, addressing complex solubility and efficiency of the oxygen evolution process.

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Footnotes

† Compound **6** has satisfactory analytical and spectroscopic data, and was produced as a single rotamer, presumably with the aldehyde

functions *trans*-related as drawn: δ (^{1}H, 300 MHz, $CDCl_3$) 3.82 (6 H, s), 6.58 (2 H, d, *J* 8.6 Hz), 7.16 (2 H, dd, *J* 2.4 and 8.6 Hz), 7.32 (2 H, d, *J* 2.3 Hz), 7.38 (2 H, dd, *J* 1.2 and 7.0 Hz), 7.55 (2 H, t, *J* 7.0 Hz), 7.96 (2 H, dd, *J* 1.3 and 8.3 Hz), and 10.29 (2 H, s).

‡ Compound **7** had satisfactory analytical and spectroscopic data: δ (^{1}H, 300 MHz, $CDCl_3$) 6.63 (2 H, d, *J* 8.0 Hz), 7.05–7.21 (4 H, br m), 7.43 (2 H, dd, *J* 1.3 and 7.1 Hz), 7.59 (2 H, t, *J* 7.1 Hz), 9.63 (2 H, s), and 10.77 (2 H, s).

§ Compound **8** was prepared as follows: To aldehyde **7** (30 mg, 0.08 mmol) in CH_2Cl_2–MeOH (1 : 1, 20 ml) was added $Mn(ClO_4)_2{\cdot}6H_2O$ (**CAUTION**! Explosive perchlorate) (29 mg, 0.08 mmol) and K_2CO_3 (44 mg, 0.32 mmol). A yellow precipitate was produced which was treated with 1,3-diaminopropane (6 mg, 0.08 mmol) in MeOH (2 ml). After 5 d, a green precipitate was formed and unreacted K_2CO_3 was removed by filtration. The resulting mixture was evaporated, washed with water and acetone (2×), and dried over P_2O_5 to give complex **8** (45%): υ/cm^{-1} (KBr) 3250 (br, coord. H_2O), 1621 (st, C=N), 1080 (br, unsplit, uncoord. ClO_4), 540 (w, Mn–O), and 450 (w, Mn–N); *m/z* (FAB) 919 ($C_{54}H_{40}N_4O_4Mn_2{}^+$) and 834 ($C_{54}H_{43}N_4O_4Na$); accurate mass, $C_{54}H_{40}N_4O_4Mn_2$ requires *m/z* 919.1889, found peak at *m/z* 919.1897.

¶ Oxygen evolution was monitored as previously reported,[3] using a degassed suspension of complex **8** (180 mg, 0.015 mmol), *p*-benzoquinone (490 mg, 4.54 mmol) in water (450 ml).

References

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5 For examples, see R. F. Heck, *Palladium Reagents in Organic Chemistry*, Academic Press, New York, 1985, ch. 6.