New Unsymetrical Manganese(II,III) Dimer as Electron Donor in Artificial Photosynthesis
Part 2. Photochemistry and spectroscopy

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A new dinuclear manganese complex ($[Mn_2L(\mu\text{-}OAc)_2]\cdot ClO_4$) **2**, has been synthesized, where L is the anion of 2-(N,N-Bis(2-methylpyridyl)aminomethyl)-6-(N-(3,5-di-tert-butylbenzyl-2-hydroxy)-N-(pyridylmethyl)aminomethyl)-4-methylphenol. The two coordinated manganese ions are bridged via two bidentate acetate groups and the 4-methylphenolate group of the ligand. Pulsed and cyclic voltammetry, in combination with bulk electrolysis and EPR spectroscopy, revealed that the Mn_2(II,III) complex undergoes three metal-centered, reversible to quasi-reversible processes in dry acetonitrile. The reduction to Mn_2(II,II) at $E_{1/2} = -0.53$ V vs. Fc^+/Fc^0 and oxidation to the Mn_2(III,III) state at $E_{1/2} = 0.38$ V, are both fully reversible. A second, quasi-reversible oxidation process at $E_{1/2} = 0.755$ V vs. Fc^+/Fc^0 becomes reversible at faster scan rates. The reaction product was short-lived however. As chemical reversibility was obtained for scan rates of $v \geq 10$ Vs^{-1}, a lower limit of the lifetime of the divalent oxidation product of about 100 ms could be estimated. The product of the second oxidation wave could thus not be isolated by bulk electrolysis.

We investigated if a product of 2-electron oxidation could be isolated by flash photolysis by **2** in partly aqueous solution, using Ru(II)-trisbipyridine as photosensitizer and Co(III)-pentaamminechloride as electron acceptor. The EPR spectrum revealed that **2** was then successively oxidized first to Mn_2(III,IV) and then further oxidized to an EPR -silent species. Cyclic voltammetry in solutions with 10% (v:v) water reveal a first oxidation wave peaking at $E_{ox} = 0.2$ V vs. Fc^+/Fc^0 as before.However, the second oxidation appeared already at 0.6V. In addition a third oxidation was observed at ca 0.9 V vs. Fc^+/Fc^0. These results indicate that the original complex **2** reacts with water in a way that allows forming higher oxidation states at lower redox potentials than in dry acetonitrile. Implications for structural changes are discussed.

Synthesis and chrystal structure caracterization are presented in a separate contribution by Magnus Anderlund et al.