New Unsymetrical Manganese(II,III) Dimer as Electron Donor in Artificial Photosynthesis

Part 1. Synthesis and Carracterisation

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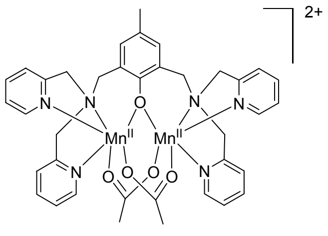
A new dinuclear manganese complex ($[Mn_2L(\mu\text{-}OAc)_2]\cdot ClO_4$) **2**, has been synthesized, where L is the anion of 2-(N,N-Bis(2-methylpyridyl)aminomethyl)-6-(N-(3,5-di-tert-butylbenzyl-2-hydroxy)-N-(pyridylmethyl)aminomethyl)-4-methylphenol. The two coordinated manganese ions are bridged via the two bidentate acetate ligands and the 4-methylphenolate group of the ligand. The $[Mn_2L(\mu\text{-}OAc)_2]\cdot ClO_4$ complex crystallizes in a monoclinic system, and the two manganese ions have symmetry properties consistent with a Mn_2(II,III) dimer which was confirmed by EPR spectroscopy. The crystal structure of **2** was compared with the crystal structure of **1** and **3**.

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 oxidation process at $E_{1/2} = 0.755$ V vs. Fc^+/Fc^0 becomes reversible at faster scan rates. The shift of potential in the redox chemistry of **2** compared to **1** and **3** has been studied.

Spectroscopic carracterisation and photochemical reactions are presented in a separate contribution by Ann Magnuson et al..



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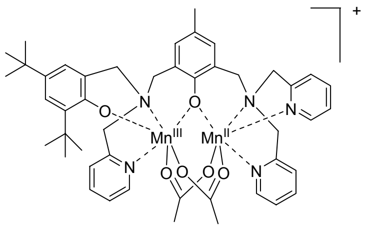

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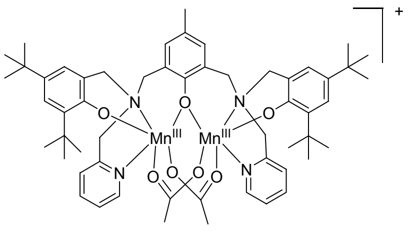

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