Water Oxidation Catalyzed by a Dimanganese Bis(μ-oxo) Complex

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Functional model complexes of the oxygen-evolving center (OEC) are important because they can help us understand precisely how the OEC oxidizes water to oxygen. This knowledge can then be applied to oxidation catalysts for water splitting. Though there are many known catalytic systems for oxidizing water, very few of them bear a close resemblance to the OEC, which features an arrangement of μ-oxo bridged dimanganese cores and performs one-electron oxidations. In this work, I report water oxidation ability of a TPA-bound, μ-oxo dimanganese complex. Unlike related dimanganese complexes, this complex has no vacant sites for binding water and so its oxidation ability must arise from the oxygen atoms bound in the rhombic core itself. The complex forms part of a system that uses Ce^{IV} as one-electron receiver. The system functions stoichiometrically in solution or catalytically when the complex is adsorbed on montmorillonite clay. The catalytic turnover frequency (TOF = 1.25/10 min) of the clay-adsorbed system is the highest value for a water oxidation manganese catalyst yet reported.

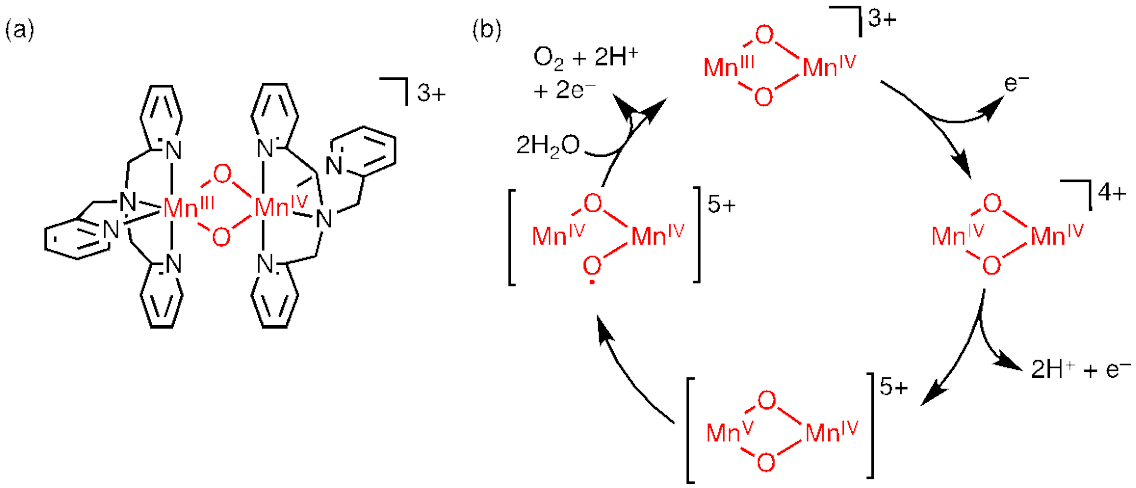

Figure 1. (a) The structure of dimanganese bis(μ-oxo) complex and (b) proposed catalytic cycle for water oxidation of the complex with Ce^{IV}.