

A novel $[\text{Mn}^{\text{III}}(\mu\text{-O})(\mu\text{-OH})(\mu\text{-OAc})\text{Mn}^{\text{III}}]^{2+}$ core. Synthesis, characterisation and proton-coupled electron transfer properties

S MAHAPATRA, T K LAL and R N MUKHERJEE*

Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India

The active site for water oxidation in photosystem II (PS II) consists of a polynuclear manganese oxo aggregate which undergoes sequential electron transfer steps. Many proposed mechanisms for water oxidation involve protonation-deprotonation at the bridged oxo groups with concomitant oxidation or reduction of the metal centres. Systematic investigation on net H atom transfer to the bridging oxo groups of synthetic manganese complexes thereby seem fruitful in attempting to reach a better understanding of the redox cycle of PS II. In the present work, detailed electrochemical studies were carried out using two model complexes having core structures $[\text{Mn}^{\text{IV}}(\mu\text{-O})_2(\mu\text{-OAc})\text{Mn}^{\text{III}}]^{2+}$ and $[\text{Mn}^{\text{III}}(\mu\text{-O})(\mu\text{-OH})(\mu\text{-OAc})\text{Mn}^{\text{III}}]^{2+}$ to demonstrate, for the first time, facile redox transformations between the manganese oxidation levels. The complexes with terminal ligands, methyl{2-(2-pyridyl)ethyl}-(2-pyridyl-methyl)amine were characterised using infrared and absorption spectroscopy via variable-temperature magnetic susceptibility measurements. Dimanganese(IV, III) complexes were characterised by their unique EPR structural properties.

*For correspondence