Determination of Ligand Exchange Rates in di-μ-oxo di-Manganese Complexes by Electrospray Ionization Mass Spectroscopy

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Photosynthetic oxygen evolution converts two H_2O molecules into O_2. The mechanisms proposed in the literature involve the binding of H_2O as terminal ligands to Ca and/or Mn atoms in the oxygen evolving complex (OEC) of photosystem II (PSII). The H_2O are proposed to undergo oxidation either while bound as terminal ligands or via incorporation into μ-oxo bridges between Mn atoms. Information on the structure of the H_2O bound in the OEC has been obtained from measurements of the rates of isotope exchange between substrate H_2O and bulk $H_2{}^{18}O$.[1]

Investigation of H_2O exchange in model complexes will help to provide a basis for interpretation of biological experiments, and may reveal the nature of H_2O-binding sites in the OEC. There have been measurements of the rate of H_2O exchange in $[Mn(H_2O)_6]^{2+}$ (rate constant ~ 2×10^7 s^{-1}).[2] To date, however, no ligand exchange rates on high valent oxomanganese complexes have been determined, although exchange of the μ-O bridges has been demonstrated in a di-μ-O Mn_2(III/IV) dimer and a mono-μ-O Mn_2(III/III) dimer.[3]

We report here the use of a time-resolved mass spectrometric technique in the measurement of μ-O and terminal H_2O ligand exchange rates in $[L_2Mn_2^{III/IV}(\mu\text{-}O)_2(H_2O)_2](NO_3)_3$ (**1**)**,** where L = 4′-mesityl-2,2′:6′,2′′-terpyridine) and μ-O and μ-OAc ligand exchange rates in $L'_2Mn_2^{III/IV}(\mu\text{-}O)_2(\mu\text{-}OAc)](ClO_4)_2$ (**2**) and $L'_2Mn_2^{IV/IV}(\mu\text{-}O)_2(\mu\text{-}OAc)](ClO_4)_3$ (**2′**), where L′ = bis(2-pyridyl)ethylamine. A comparative study of these complexes allows us to look at the effects of structural changes and oxidation state changes on the rates of ligand exchange. This is the first measurement of ligand exchange rates on biologically relevant high-valent Mn compounds.

References

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