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$_2$O molecules into O$_2$. The mechanisms proposed in the literature involve the binding of H$_2$O as terminal ligands to Ca and/or Mn atoms in the oxygen evolving complex (OEC) of photosystem II (PSII). The H$_2$O 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$_2$O bound in the OEC has been obtained from measurements of the rates of isotope exchange between substrate H$_2$O and bulk H$_2^{18}$O.\(^1\)

Investigation of H$_2$O exchange in model complexes will help to provide a basis for interpretation of biological experiments, and may reveal the nature of H$_2$O-binding sites in the OEC. There have been measurements of the rate of H$_2$O exchange in [Mn(H$_2$O)$_6$]$^{2+}$ (rate constant $\sim 2 \times 10^7$ 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$_2$O ligand exchange rates in [L$_2$Mn$_2^{III/IV}$ (µ-O)$_2$(H$_2$O)$_2$](NO$_3$)$_3$ (1), where L = 4'-mesityl-2,2':6',2''-terpyridine) and µ-O and µ-OAc ligand exchange rates in L'$_2$Mn$_2^{III/IV}$ (µ-O)$_2$(µ-OAc)](ClO$_4$)$_2$ (2) and L'$_2$Mn$_{IV/IV}$ (µ-O)$_2$(µ-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