Water oxidation catalyzed by a dinuclear Mn complex

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A dimanganese(II) bis-aquo complex \([\text{Mn}_2(\text{cmep})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2\), (cmep\(^-\) = N-carboxymethyl-N’-methyl-N,N’-bis(2-pyridylmethyl)-1,2-ethandiamine),\(^1\) catalyzes the oxidation of water by \(^{t}\)butylhydrogenperoxide (TBHP) to dioxygen with many turnovers and without degradation. \(^{18}\){\textsuperscript{O}} isotope labelling shows the reaction is highly specific: One oxygen atom in the product dioxygen is derived from water, the other is derived from the TBHP. Membrane Inlet Mass Spectrometry (MIMS) was used to measure the concentration of evolved \(\text{O}_2\) directly \(\text{in solution}\). Transient higher-valent intermediates in a proposed mechanism, dinuclear Mn\(^{\text{III}}\)-Mn\(^{\text{III}}\) and Mn\(^{\text{IV}}\)-Mn\(^{\text{IV}}\) oxo-bridged complexes have been identified (UV-Vis, ESI MS, CV). It is therefore proposed that in the catalyst cycles between a Mn\(^{\text{II}}\)-Mn\(^{\text{II}}\) state with the substrate, two waters, bound, and a dioxo-bridged Mn\(^{\text{IV}}\)-Mn\(^{\text{IV}}\) complex as depicted. The core of this latter species is presumably a precursor for the evolved dioxygen. The pentadentate carboxylate-containing ligand provides the flexibility to support coordination number and oxidation state changes required for a proposed mechanism. The carboxylate groups concurrently shifts between bridging to terminal to non-coordinated during the process.

\[2 \text{BuOOH} \rightarrow 2 \text{H}_2\text{O} + 2 \text{O}_2\]

\[2 \text{BuOH} + 2 \text{H}_2\text{O} \rightarrow 2 \text{BuOOH}\]