Mimicking class Ib dimanganese ribonucleotide reductase

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A fascinating facet of ribonucleotide reductase’s (RNRs) Chemistry has been the identification of a dimanganese (Mn$_2$) active site in class Ib RNRs that requires superoxide anion (O$_2^-$), rather than dioxygen (O$_2$), to access a high-valent Mn$^{III}$Mn$^{IV}$ oxidant via a Mn$^{II}$Mn$^{III}$-peroxide precursor (see scheme). We have prepared two Mn$^{II}_{2}$ complexes that, upon exposure to KO$_2$, yield Mn$^{II}$Mn$^{III}$-peroxide adducts. Activation of the Mn$^{II}$Mn$^{III}$-peroxide complexes either via thermal decay or acid-activation results in meta-stable Mn$^{III}$Mn$^{IV}$ adducts. The Mn$^{II}$Mn$^{III}$-peroxide complexes displayed electronic absorption features typical of a Mn-peroxide species, and either a 29- or 22-line EPR signal typical of a Mn$^{II}$Mn$^{III}$ entity. The Mn$^{II}$Mn$^{IV}$ adducts displayed electronic absorption features typical of a Mn$^{III}$Mn$^{IV}$ species, and 16-line EPR signal typical of a Mn$^{II}$Mn$^{IV}$ entity. Electrospray ionisation mass spectrometry (ESI-MS) confirmed the elemental composition of the Mn$^{II}$Mn$^{III}$-peroxides and Mn$^{II}$Mn$^{IV}$ complexes. While the Mn$^{III}$Mn$^{III}$-peroxides were unreactive towards weak O–H bonds (as those found in tyrosine), the Mn$^{III}$Mn$^{IV}$ complexes were found to be efficient oxidants, capable of phenol O–H bond activation via ratelimiting electron transfer. Our findings provide comprehensive support for the postulated mechanism of O$_2$ activation at class Ib Mn$_2$ RNRs.

References: