Protonation of [{Mn^{IV}(saltn)(μ_2-O)}$_2$] Results in Significant Modification of Structure and Catalase-like Reactivity†

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Protonation of an {Mn^{IV}(μ_2-O)}$_2$ core to form {(Mn^{IV})$_2$(μ_2-O)(μ_2-OH)} leads to perturbations of the physical properties of this unit including an increase in metal–metal separation (*ca.* 0.1 Å) and loss of catalase reactivity.

Manganese is an essential component of numerous biological redox activities including catalase reactions[1] and the oxidation of water to dioxygen in photosynthesis.[2] In both processes manganese is organized either as a dimer or as a higher-nuclearity cluster. One important structural constraint elucidated through EXAFS spectroscopy[3] and model complex studies[4] is that high-valent manganese (+3 and +4) complexes often exhibit 2.7 Å Mn–Mn separations that are best explained by di-μ_2-O^{2-} linkages in {MnO}$_2$ cores. As shown in eqns. (1) and (2), both reactions require changes in the protonation state of the substrate.

$$2H_2O_2 \rightarrow O_2 + 2H_2O \quad (1)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (2)$$

Such proton rearrangements might be facilitated by the oxo groups in these multinuclear assemblies. Therefore, an understanding of the structural perturbations and modifications of physical properties coupled to protonation of {MnO}$_2$ cores would provide valuable insight into mechanistic proposals for catalysis. Unfortunately, a comparison of unprotonated[5] and protonated[6] complexes has been reported for only one tetranuclear system. In this case, a significant bond elongation was associated with protonation and the complex, which originally was very robust, became markedly more reactive. In this report we describe the conversion of an {Mn^{IV}(μ_2-O)}$_2$ core to a stable {(Mn^{IV})$_2$(μ_2-O)(μ_2-OH)}$^+$ form which has dramatically different reactivity with hydrogen peroxide.

The dinuclear [{Mn^{IV}(μ_2-O)(saltn)}$_2$] **1** can be prepared in quantitative yield by the reaction of [Mn^{III}(saltn)(acac)] with hydrogen peroxide in acetonitrile.[7] The complex has been characterized by X-ray crystallography which revealed an Mn–Mn separation of 2.71 Å.[8] This complex has been shown to catalyse efficiently the disproportionation of hydrogen peroxide [reaction (1)] in methylene chloride.[9] Compound **1** can be protonated in methylene chloride by stoichiometric addition of one equivalent of pyridinium perchlorate to yield [{Mn^{IV}(saltn)}$_2$(μ_2-O)(μ_2-OH)]ClO$_4$ **2**.‡ The conversion of **1** to **2** can be monitored by UV–VIS spectroscopy. A shift from **1** (λ_{max} 490 nm; ε 680 dm^3 mol^{-1} cm^{-1}) to **2** (λ_{max} 520 nm; ε 754 dm^3 mol^{-1} cm^{-1}) with an isosbestic point at 463 nm is seen. Stoichiometric addition of base quantitatively regenerates **1**. The cyclic voltammogram of **2** shows a quasi-reversible reduction at +350 mV. This potential is 440 mV more positive than those for **1** illustrating that the Mn^{IV} oxidation level is destabilized upon protonation at the oxo bridge. This is expected based on a decrease in ligand basicity of the oxo linkage.

Fig. 1 illustrates the Fourier transforms of the EXAFS spectra§ for compounds **1** and **2** and for the Mn^{III} dimer[7] [{Mn^{III}(μ_2-OMe)(saltn)}$_2$] **3** which has an Mn–Mn separation of 3.19 Å as determined crystallographically. The best fits to the EXAFS spectra of **1** and **3** give Mn–Mn separations of 2.71 and 3.19 Å, respectively. Analysis of the spectrum of **2** gives an Mn–Mn separation of 2.81 Å. Again, this is consistent with a decrease in donation of the bridging ligand. We have described[8] a correlation between bond length and bond angle for Mn^{IV}–(μ_2-O^{2-})–Mn^{IV} model systems. Based on this analysis, the Mn–O–Mn angle increases from 98° to *ca.* 102° on going from **1** to **2**. We would also expect an elongation of the manganese to oxygen bond for the Mn–OR linkage although we cannot determine this distance at the moment. Preliminary magnetic studies are consistent with these observations, showing an increase in the magnetic moment of **2** (2.3 μ_B at 100 K) from that of **1** (0.88 μ_B) consistent with decreased antiferromagnetic exchange. Detailed analysis of variable temperature magnetic susceptibilities to evaluate this proposal will be presented separately.

While **1** will immediately catalyse hydrogen peroxide dismutation in a catalase reaction, solutions of **2** exhibit a significant lag period before this catalase activity occurs and then only reach a maximum rate of half that predicted for **1** based on total manganese. However, **2** will react with sodium hydroperoxide with the same efficiency as **1** reacts with H_2O_2. These observations are consistent with a model whereby **2**

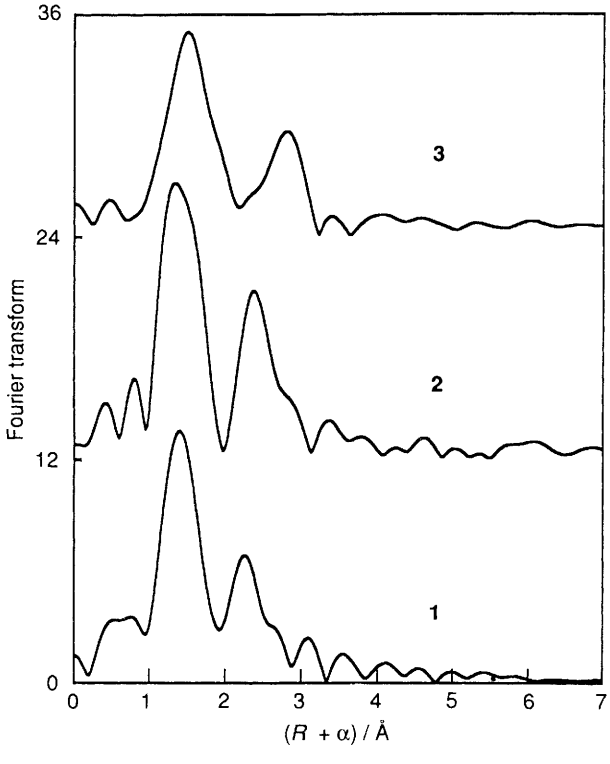

Fig. 1 Fourier transforms of EXAFS spectra of **1**, **2** and **3**. Plots were obtained over the range 3–12 K. Spectra of **2** and **3** are offset by 12 and 24 units for clarity.

† H_2saltn = 1,3-bis(salicylideneaminato)propane: Hacac = pentane-2,4-dione.

‡ Found: C, 50.6; H, 3.9; N, 6.9; Mn, 12.5; Cl, 4.7. Calc. for $C_{34}H_{33}Mn_2N_4O_{10}Cl$: C, 50.85; H, 4.1; N, 6.9; Mn, 13.7; Cl 4.4%.

§ Spectra measured in transmission using NSLS line X10C. Quantitative curve-fitting analysis used theoretical amplitude and phase parameters for Mn–Mn scattering,[10] with the scale factor and ΔE_0 calibrated by fitting compounds of known structure. No significant improvement was seen if a second shell of C-scatterers was added.

does not react directly with H_2O_2. Rather a small proportion becomes deprotonated to give **1** (the efficient catalase mimic). Mn^{III}(saltn)(OH) and Mn^{III}(saltn)(H_2O) are the initial products when hydrogen peroxide reacts with **1** in the presence of one equivalent of acid. The Mn^{III}(saltn)(OH) can react further with H_2O_2 to reform **1** while Mn^{III}(saltn)(H_2O) is unreactive with H_2O_2.[7] Thus, beginning with two equivalents of **2**, one slowly and progressively obtains one equivalent of **1**. These reactions are shown as eqns. (3)–(5). This series of events explains both the lag phase (due to the slow build-up of the reactive species **1**) and final rates that are 50% of the levels predicted based on total manganese.

$$\underset{\mathbf{2}}{2[\{Mn^{IV}(saltn)\}_2(\mu_2\text{-}O)(\mu_2\text{-}OH)]^+} \rightarrow \underset{\mathbf{1}}{2[\{Mn^{IV}(\mu_2\text{-}O)(saltn)\}_2]} + 2H^+ \quad (3)$$

$$2[\{Mn^{IV}(\mu_2\text{-}O)(saltn)\}_2] + 2H^+ + 2H_2O_2 \rightarrow 2O_2 + 2[Mn^{III}(saltn)(OH)] + 2[Mn^{III}(saltn)(H_2O)]^+ \quad (4)$$

$$2[Mn^{III}(saltn)(OH)] + H_2O_2 \rightarrow [\{Mn^{IV}(\mu_2\text{-}O)(saltn)\}_2] + 2H_2O \quad (5)$$

Clearly, the protonation state of this manganese oxo core is critical to the capacity to act as a catalyst and presumes that such considerations are also essential in the biological milieu. It is worth considering why **1** can be protonated and is an efficient catalase while previous $\{Mn^{IV}(\mu_2\text{-}O)\}_2$ complexes have not been reported to show similar chemistry. In most cases, the $\{Mn^{IV}(\mu_2\text{-}O)\}_2$ core is found in systems that contain neutral nitrogen donor ligands.[11] Recent electrochemical studies of such compounds[12] have shown pK_a values of *ca.* 11 for $\{Mn^{III}(\mu_2\text{-}OH)(\mu_2\text{-}O)\}_2$ and *ca.* 2 for $\{Mn^{III}Mn^{IV}(\mu_2\text{-}OH)(\mu_2\text{-}O)_2\}$. The anionic charge and stronger donor ability of phenolates as compared to pyridine and related ligands leads to more electron density on the metal centres. Therefore, the oxo bridges are not required to donate as much electron density to the metal centre and can be involved in proton acceptor chemistry. This would suggest that enzymes that incorporate a highly oxygen-rich ligand environment require a high-valent catalytic cycle while those with a nitrogen-rich environment proceed through lower-valent metal centres.

The authors acknowledge support from NIH [grants 39406 (V. L. P.) and 38047 (J. P. H.)], an Amoco Research Fellowship to E. J. L., a Molecular Biophysics Training Award to P. J. R. and Alfred P. Sloan Fellowships to J. P. H. and V. L. P.

Received, 23rd September 1991; Com. 1/04892I

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