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LETTER

Formation of Mn_2(III/IV) species in reaction mixtures of hydrogen peroxide and binuclear Mn_2(II/II) or Mn_2(II/III) compounds

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The oxidation of water by photosynthetic organisms results in the release of molecular oxygen into the atmosphere, a process on which all animal life is dependent. In this process the primary photochemical reaction produces a strong oxidant that is not capable of directly catalyzing the four-electron oxidation of water. Instead this is accomplished by a complex comprised of four manganese ions believed to be associated in the form of a ligand-bridged cluster [1]. In 1982, Nishida and co-workers reported that some manganese(III) complexes with a μ-alkoxo bridge exhibit a high catalase-like function. Since our report, the presence of Mn catalase has been reported for several biological systems [3], and it has been generally accepted that these Mn catalases contain a binuclear Mn site [4]. Interestingly, it is well known that the manganese cluster in the photosystem also exhibits a catalase-like function [5]. It vigorously disproportionates the added H_2O_2 in the dark following the formation of the S_2 state by a single flash. The mechanism may involve an initial two-electron reduction ($S_2 \rightarrow S_0$) with O_2 formation followed by re-oxidation to the S_2 state with H_2O release [6]. These facts suggest that a study on the catalase-like function of the polymeric manganese cluster would be very useful in elucidating the function of manganese ions in both these enzymes. In this article we report our preliminary but very interesting results on this problem.

The binuclear manganese compounds used in this study are as follows:

Binuclear Mn_2(II/II):

Mn_2(L-py)$Cl_2(H_2O)_2PF_6$ [7]
Mn_2(L-py)$(CH_3COO)_2PF_6$ [8]

Binuclear Mn_2(II/III):

Mn_2(L-py)$(CH_3COO)_2(PF_6)_2$ [9]

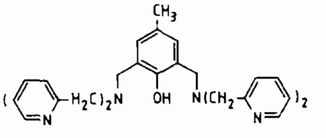
Binuclear Mn_2(III/III):

Mn_2(L-pac)$(CH_3COO)_2Na$ [10]
Mn_2(L-5-Sal)$(CH_3COO)(OCH_3)ClO_4$ [11]

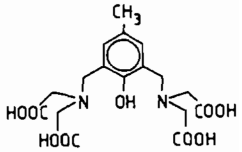
Binuclear Mn_2(III/IV) with di-μ-oxo bridge:

$Mn_2O_2L_2\ (ClO_4)_3$, L = cyclam [12]
tris(2-pyridylmethyl)amine [13]
N,*N'*-bis(2-pyridylmethyl)-ethylenediamine [14]

The chemical structures of some of the ligands are given below.



H(L-py)



H_5(L-pac)

When an acetonitrile solution of Mn_2(II/II)(L-py)$Cl_2(H_2O)_2PF_2$ was mixed with an acetonitrile solution of H_2O_2 (commercial 30% H_2O_2 was diluted by acetonitrile), the colorless solution turned to dark brown (cf. Fig. 1), and the drastic change was also observed in the ESR spectra (cf. Fig. 2). The ESR signal pattern in Fig. 2, i.e. the presence of a '16-line ESR signal', suggests that a binuclear Mn_2(III/IV) species exists in the brown solution [15]. We

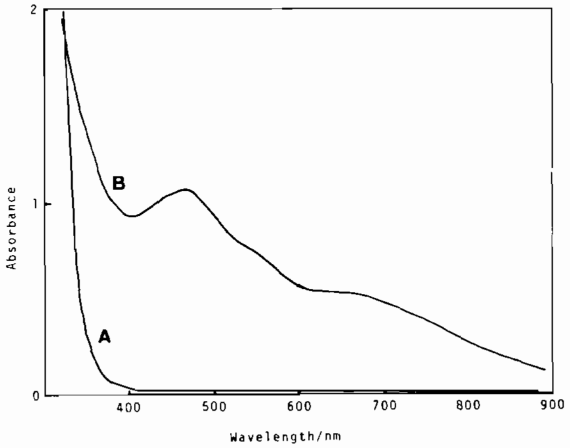


Fig. 1. Absorption spectra of Mn complex solutions (25 °C, in acetonitrile). A: Mn_2(II/II)(L-py)$Cl_2(H_2O)_2PF_6$ (1/1000 M). B: Equivolume mixture of Mn_2(II/II)(L-py)$Cl_2(H_2O)_2PF_6$ (1/1000 M) and H_2O_2 (1/50 M).

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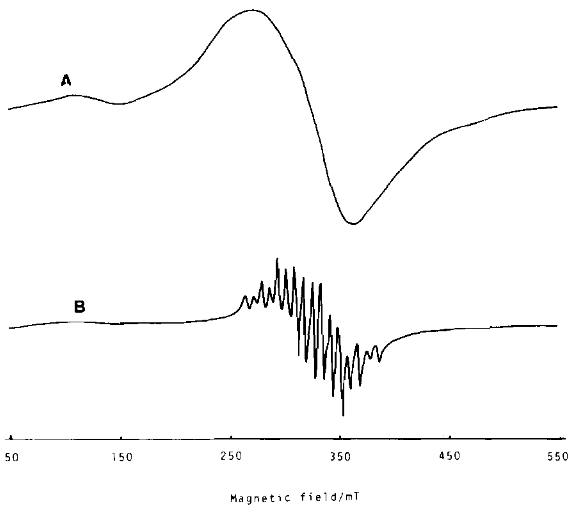

Fig. 2. ESR spectra of Mn complex solutions (77 K, X-band, in acetonitrile). A: $Mn_2(II/II)(L\text{-}py)Cl_2(H_2O)_2PF_6$ (1/1000 M). B: Equivolume mixture of $Mn_2(II/II)(L\text{-}py)Cl_2(H_2O)_2PF_6$ (1/1000 M) and H_2O_2 (1/50 M).

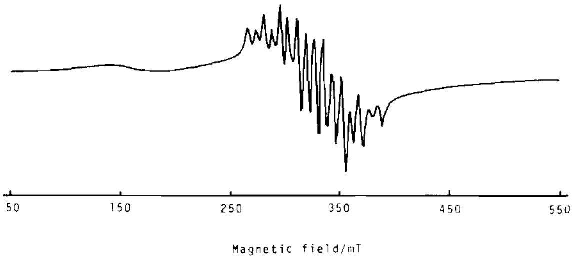

Fig. 3. ESR spectrum (77 K, X-band, in acetonitrile) of equivolume mixture of $Mn_2(II/III)(L\text{-}py)(CH_3COO)_2(PF_6)_2$ (1/1000 M) and H_2O_2 (1/50 M).

also observed that decomposition of H_2O_2 proceeds in this binuclear Mn(II) complex solution, suggesting a 'catalase-like function' of $Mn_2(II/II)(L\text{-}py)Cl_2(H_2O)_2{}^+$. Interestingly, the changes in absorption and in the ESR spectra found for the above complex solution, were not observed for the solution of H_2O_2 and binuclear manganese(II) complex, $Mn_2(II/II)(L\text{-}py)(CH_3COO)_2PF_6$. In addition to this, the addition of methanol or $(C_2H_5)_4NCl$ to an acetonitrile solution of $Mn_2(II/II)(L\text{-}py)Cl_2(H_2O)_2PF_6$ did inhibit the changes in the absorption and ESR spectra.

Similar absorption and ESR spectral changes were also observed when an acetonitrile solution of $Mn_2(II/III)(L\text{-}py)(CH_3COO)_2(PF_6)_2$ was mixed with H_2O_2 in acetonitrile, i.e. the ESR spectrum (see Fig. 3) of the resulting brown solution is almost the same as that observed for the $Mn_2(II/II)(L\text{-}py)Cl_2(H_2O)_2{}^+$ system. In this case the addition of methanol to the solution also inhibited the changes in absorption and in the ESR spectra. When the binuclear $Mn_2(III/III)(L\text{-}pac)(CH_3COO)_2{}^-$ complex in methanol was treated with H_2O_2 (in methanol), decoloration of the original complex occurred, indicating that the manganese(III) ions are reduced to the manganese(II) state by H_2O_2. But, the Mn(II) species thus formed did not react further with H_2O_2, similar to the case of $Mn_2(II/II)(L\text{-}py)(CH_3COO)_2PF_6$. All the $Mn_2(III/IV)$ complexes used in this study did not react with H_2O_2, however, these compounds reacted with superoxide anion, yielding a Mn(III) species. This implies that H_2O_2 is acting as a two-electron donor and/or acceptor in these reactions.

The Mn catalase from *Thermus thermophilus* has been extensively studied [6]. It has been reported that four oxidation states of this enzyme have been produced; $Mn_2(II/II)$, $Mn_2(II/III)$, $Mn_2(III/III)$ and $Mn_2(III/IV)$, and two mixed valence states which are inactive in H_2O_2 disproportionation. Although the atomic structure of the coordination environments of the Mn catalase is not known, a minimal mechanism for peroxide disproportionation has been inferred from the ESR spectral data [6]. An elaboration of this mechanism to include the inferred coordination requirement is given in Fig. 4 [16]. It is analogous to the mechanism found for a synthetic $Mn_2(II/II)$ complex [17]. The $Mn_2(II/II)$ state of the thermus enzyme undergoes a facile ligand substitution reaction involving a variety of small anions (Cl^-, F^-, $N_3{}^-$ and $H_2PO_4{}^-$), all of which inhibit the reaction with peroxide [6].

Several assumptions may be made from the results given in Fig. 4. The fact that the catalase-like function was observed for $Mn_2(II/II)(L\text{-}py)Cl_2(H_2O)_2{}^+$, but not for $Mn_2(II/II)(L\text{-}py)(CH_3COO)_2{}^+$, demonstrates the necessity of a coordination of water molecule in the binuclear Mn compound, and is consistent with the assumption of species B in Fig. 4. The inhibition by Cl^- (addition of $(C_2H_5)_4NCl$) observed in this work seems to be coincident with the presence

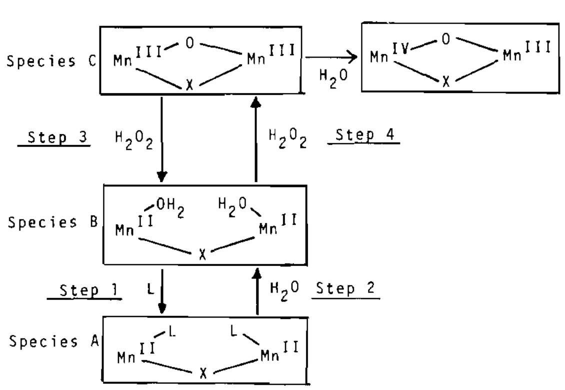

Fig. 4. Assumed mechanism of manganese catalase [6]: L is ligand such as Cl^- and acetate, etc.; X is an unknown bridging group.

of step 1 in Fig. 4. The inhibition by acetate ion observed for the thermus enzyme is also consistent with the fact that $Mn_2(II/II)(L\text{-}py)(CH_3COO)_2^+$ is inactive for H_2O_2 disproportionation. It should be noted here that our results clearly indicate that the mixed valence state complex, $Mn_2(II/III)(L\text{-}py)(CH_3COO)_2^{2+}$ can interact with H_2O_2 in acetonitrile solution, which is quite different from that observed for the thermus enzyme [6].

It is well known that a mixed valence species of $Mn_2(III/IV)$ states forms in the reaction mixture of a binuclear $Mn_2(III/III)$ complex with a μ-oxo bridge and H_2O [18]. This explains the observed fact that a $Mn_2(III/IV)$ species is present in the reaction mixture of $Mn_2(II/II)(L\text{-}py)Cl_2(H_2O)_2^+$ and H_2O_2, which should be formed according to the following scheme (cf. also Fig. 4)

$$Mn_2(II/II) \longrightarrow$$
$$Mn_2(III/III), \text{ with } \mu\text{-oxo bridge} \longrightarrow Mn_2(III/IV)$$

In the case of $Mn_2(II/III)(L\text{-}py)(CH_3COO)_2^{2+}$ and H_2O_2, the reason for the formation of a $Mn_2(III/IV)$ species is a problem to be solved in future work.

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