Geometrical Significance of a μ-Phenoxo-bis(μ-carboxylato)-dimanganese Core as an Active-site Model of Manganese Catalase

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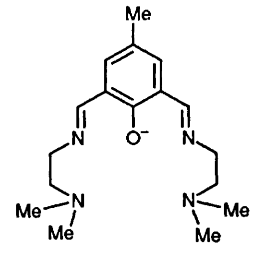
μ-Phenoxo-bis(μ-carboxylato)dimanganese(II) complexes of C_s symmetry showed a high catalyse-like activity to disproportionate hydrogen peroxide whereas those of C_2 symmetry showed only a low activity.

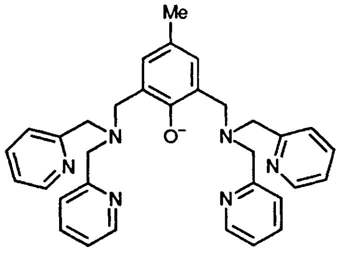
Manganese catalases from *Lactobacillus plantarum*[1] and *Thermus thermophilus*[2] are known to contain a pair of Mn ions at their active site.[3,4] The μ-oxo-bis(μ-carboxylato)dimanganese core structure is proposed as a likely candidate[5] for the active site based on visible spectral characteristics and an extended X-ray absorption fine structure (EXAFS) study.[6] However, the core structure in manganese catalase has not been established yet and the mechanism of H_2O_2 disproportionation is still unknown.

Recently we have reported that μ-phenoxo-bis(μ-carboxylato)dimanganese(II) complexes[7] derived from 2,6-bis[*N*-(dimethylaminoethyl)iminomethyl]-4-methylphenol show a catalase-like activity in dimethylformamide (dmf).[8] Two manganese(IV) intermediates of the cores $\{Mn^{IV}(=O)\}_2$ and $Mn^{II}Mn^{IV}(=O)$ have been detected in the H_2O_2 disproportionation reaction and the cycle $\{Mn^{IV}(=O)\}_2$–$\{Mn^{III}(OH)\}_2$ is proposed to be responsible for high catalase-like activity. In this communication catalase-like activity of dinuclear manganese(II) complexes has been studied in view of the geometrical feature of the core structure for three μ-phenoxo-bis(μ-carboxylato)-dimanganese(II) complexes[7,9,10] $[Mn_2L^1(PhCO_2)_2(NCS)]$ **1** $\{L^1$ = 2,6-bis[*N*-(dimethylaminoethyl)iminomethyl]-4-methylphenolate(1 −)}, $[Mn_2L^2(MeCO_2)_2(NCS)]$ **2** $\{L^2$ = 4-methyl-2,6-bis[*N*-(2-pyridylethyl)iminomethyl]-phenolate(1 −)} and $[Mn_2L^3(PhCO_2)_2]ClO_4$ **3** $\{L^3$ = 2,6-bis[bis(2-pyridylmethyl)-aminomethyl]-4-methylphenolate(1 −)}. All the complexes disproportionate H_2O_2 catalytically ($2H_2O_2 \longrightarrow O_2 + 2H_2O$), but their catalase-like activities differ significantly from each other.

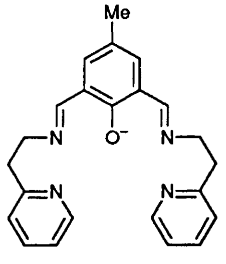
The time course of O_2 evolution by **1** is sigmoid (Fig. 1), where the initial slow reaction (*i*) and the faster reaction (*ii*) after an induction period are concerned with the disproportionation of H_2O_2.[8] In dmf **1** exists as $[Mn_2L^1(PhCO_2)_2]^+$,[8] whose molecular symmetry can be approximated as *pseudo*-C_s with the two vacant sites in *cis* positions, as depicted by the space-filling model in Fig. 2. The vacant site of one Mn [left-hand one in Fig. 2(*a*)] is significantly buried so that hydrogen peroxide preferentially interacts with the other manganese(II) ion to form $Mn^{II}Mn^{IV}(=O)$ as the final oxidation product. The H_2O_2 disproportionation catalysed by $Mn^{II}Mn^{IV}(=O)$ corresponds to the slow reaction (*i*).[8] When the complex cation $[Mn_2L^1(PhCO_2)_2]^+$ is slightly deformed, both vacant sites are available for the co-ordination of H_2O_2 to form *cis*-$\{Mn^{IV}(=O)\}_2$ as the final oxidation product. This reaction occurs after an induction period due to the necessary deformation of the precursor cation, but the *cis*-$\{Mn^{IV}(=O)\}_2$ species is more efficient in disproportionating H_2O_2 [reaction (*ii*)].



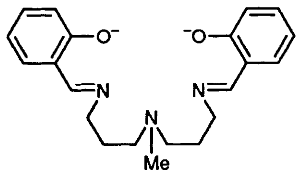
$(L^1)^-$



$(L^3)^-$



$(L^2)^-$



$(L^4)^{2-}$

Complex **2** also exists as a cation $[Mn_2L^2(MeCO_2)_2]^+$ in dmf,[9] and the time course of O_2 evolution is essentially sigmoid (Fig. 1). The initial rate by **2** is however slower than that by **1**. Further, the reaction (*ii*) by **2** occurs after a longer induction period and its rate is significantly slower when compared with that of **1** under the same conditions. The crystal structure analysis for **2** has revealed the *pseudo*-C_2 symmetry of the cation $[Mn_2L^2(MeCO_2)_2]^+$ where the sixth vacant sites of the two manganese ions are *trans* to each other (Fig. 3). Deformation of this *trans* structure (C_2 symmetry) to a *cis* structure (C_s symmetry) is essential for this complex to form *cis*-$\{Mn^{IV}(=O)\}_2$, and this seems to be difficult as gauged by the long induction period.

The initial rate of the disproportionation of H_2O_2 by complex **3** is even slower than that of **2** and reaction (*ii*) is not observed (Fig. 1). The crystal structure of the $Mn^{II}Mn^{III}$ complex of L^3, $[Mn_2L^3(PhCO_2)_2]ClO_4$, has been determined[10] (Fig. 4). The geometry around each manganese ion is six-co-ordinate but one of the Mn–N(pyridyl) bonds is

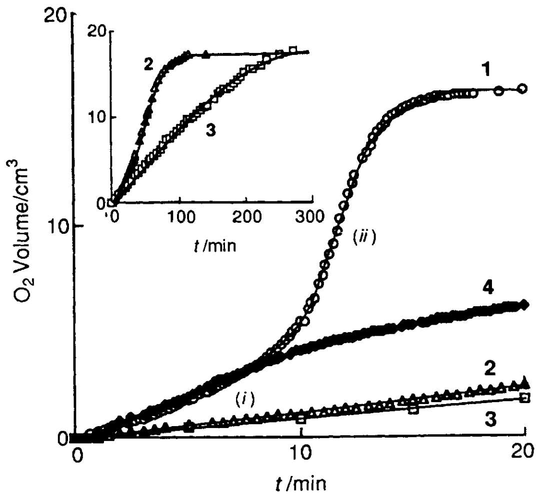
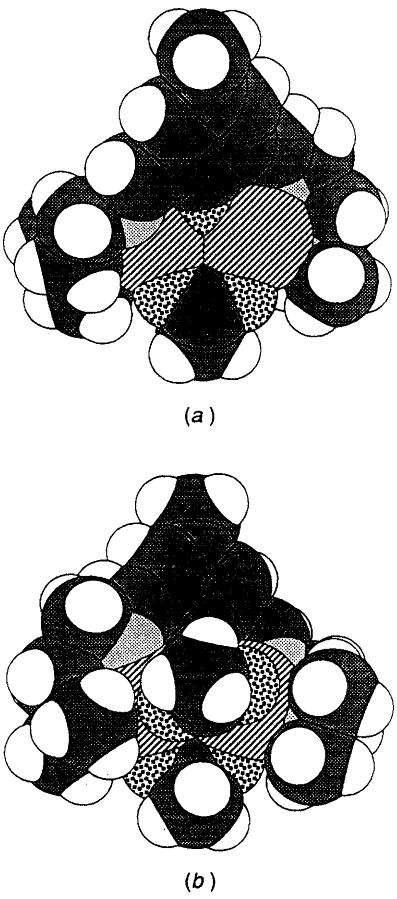


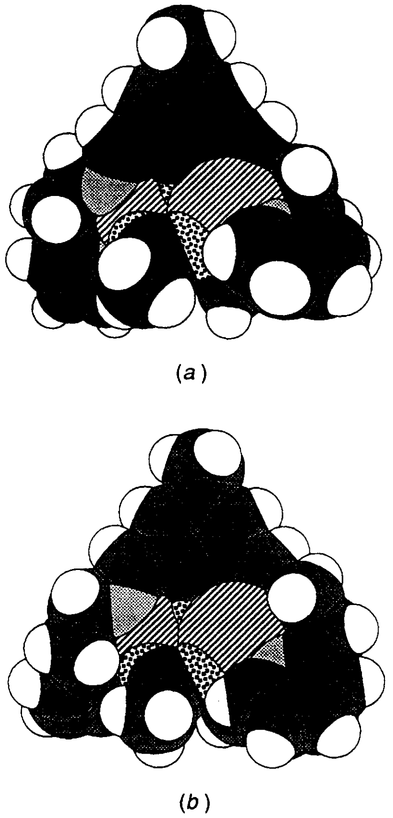
Fig. 1 Time courses of O_2 evolution in H_2O_2 disproportionation by **1** (○), **2** (△), **3** (□) and **4** (◆). Conditions: complex (10 μmol in Mn) in dmf (2 cm^3), H_2O_2 (9.9%, 0.5 cm^3; 1.45 mmol), at 0 °C


(*a*)

(*b*)

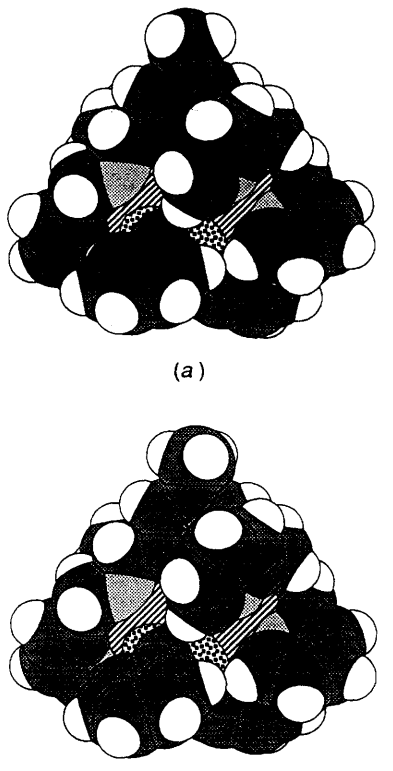
Fig. 2 Space-filling drawings of $[Mn_2L^1(MeCO_2)_2]^+$ based on the crystal structure of $[Mn_2L^1(MeCO_2)_2(NCS)]$: top- (*a*) and bottom-view (*b*). C(●), H(○), Mn(▨), N(◉), O(⁘)

elongated and this site must be available for H_2O_2 co-ordination. The two labile co-ordination sites within the Mn_2 core are *trans*, providing *pseudo*-C_2 symmetry to the $[Mn_2L^3(PhCO_2)_2]^+$ cation. The deformation of the *trans* core structure to *cis* is practically impossible because of the steric requirement of the ligand L^3, and this is consistent with the absence of reaction (*ii*) by **3**.


(*a*)

(*b*)

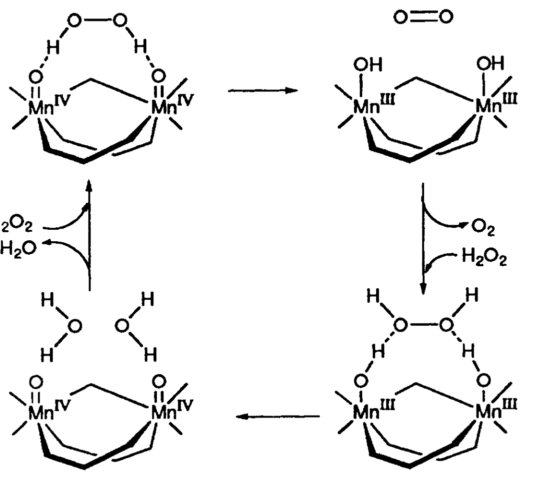
Fig. 3 Space-filling drawings of $[Mn_2L^2(MeCO_2)_2]^+$: top- (*a*) and bottom-view (*b*)


(*a*)

(*b*)

Fig. 4 Space-filling drawings of $[Mn_2L^3(PhCO_2)_2]^+$: top- (*a*) and bottom-view (*b*)

The slow reaction (*i*) therefore, is not specific for the dinuclear core structure and may be observed for mononuclear manganese complexes if they have a vacant or labile site for H_2O_2 co-ordination and a redox potential necessary for H_2O_2 disproportionation. Indeed in our experiments using the mono-



Scheme 1

nuclear manganese(III) complex $[Mn(L^4)Cl]$[11] {L^4 = *N*,*N*-bis[3-(salicylideneamino)propyl]methylamine(2−)} only the slow H_2O_2 disproportionation reaction has been observed (see Fig. 1).

From the above discussion it is evident that the *cis*-$\{Mn(=O)_2\}$ core with an appropriate Mn ··· Mn separation (*ca.* 3.3 Å) is responsible for the fast catalytic disproportionation of H_2O_2, probably through the cycle *cis*-$\{Mn^{IV}(=O)\}_2$–*cis*-$\{Mn^{III}(OH)\}_2$. This interconversion is made possible by the chelating interaction of the dinuclear manganese cores with H_2O_2 followed by prototropy (Scheme 1). Such an interconversion between the oxo and hydroxo species through prototropy is seen in oxygenation–deoxygenation processes of a haemerythrin.[12]

Synthetic oxomanganese(IV) complexes are still rare.[5,13] However, oxomanganese(IV) complexes presumably exist as intermediates in the oxidation of manganese(II) complexes but are converted into more stable di(μ-oxo)dimanganese(IV) complexes.[14] In biological manganese catalase systems it appears that the geometrical environment about the dimanganese active site is so constructed by polypeptide as to form preferentially *cis*-$\{Mn^{IV}(=O)\}_2$ (*cis*-$\{Mn^{III}(OH)\}_2$).

Acknowledgements

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