

Asymmetric Mixed Valence Manganese Complexes Containing the $[\text{Mn}^{\text{III}}(\mu\text{-O})_2(\mu\text{-MeCO}_2)\text{Mn}^{\text{IV}}]^{2+}$ Core and their Catalase Reactivity

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Two asymmetrically ligated, dinuclear, mixed valence complexes $[\text{Mn}^{\text{IV}}\text{L}(\mu\text{-O})_2(\mu\text{-MeCO}_2)\text{Mn}^{\text{III}}(\text{MeCO}_2)_2]$ **1** and $[\text{Mn}^{\text{IV}}\text{L}(\mu\text{-O})_2(\mu\text{-MeCO}_2)\text{Mn}^{\text{III}}(\text{bpy})(\text{MeOH})](\text{ClO}_4)_2 \cdot \text{MeOH}$ **2b** have been synthesized (L = 1,4,7-trimethyl-1,4,7-triazacyclononane, bpy = 2,2'-bipyridyl) and their structures have been determined by X-ray crystallography; **1** and **2b** catalyse the disproportionation of aqueous H_2O_2 .

A number of manganese containing non-haem catalases have in recent years been isolated and characterized. This important class of metalloproteins catalyse the disproportionation of hydrogen peroxide to dioxygen and water very efficiently. At present there are three such Mn catalases known; (i) one enzyme from *Lactobacillus plantarum*; ^{1a} (ii) one from *Thermophilum album* NM^{1b} and (iii) one from *Thermus thermophilus* HB8, ^{1c} all of which are thought to contain a dinuclear $\text{Mn}^{\text{III}}\text{-O-Mn}^{\text{III}}$ active site. From kinetic studies their reactivity at pH 7.0 and 25 °C has been established to be $V_{\text{max}} = 2.0 \times$

10^5 mol H_2O_2 /mol enzyme s^{-1} . Recently two reports on the catalase activity of dinuclear manganese model complexes have appeared: two dimanganese(II) complexes containing the binucleating ligand *N,N,N',N'*-tetrakis(2-methylenebenzimidazolyl)-1,3-diaminopropane-2-ol³ and $[\text{Mn}^{\text{IV}}(\mu\text{-O})(\text{salpn})_2]^{4+}$ [salpn = propane-1,2-diylbis(salicylideneaminato)]. It was shown that their catalase activity is smaller by approximately five orders of magnitude as compared with the enzymes. Since the model complexes constitute species with an identical ligand environment at both manganese ions

(symmetrical species) we decided that it would be worthwhile to synthesize and study asymmetric dinuclear species with at least one labile, easily accessible coordination site. Asymmetric model compounds of this type are a very desirable synthetic goal.⁵ We report here the syntheses, crystal structures and catalase reactivity of two such species which contain a di- μ -oxo- μ -acetate-dimanganese(III/IV) core.

Reaction of 'manganese(III) acetate', $[\text{Mn}_3^{\text{III}}(\mu\text{-MeCO}_2)_6(\mu_3\text{-O})(\text{OH}_2)_3](\text{MeCO}_2)_2$, with the macrocycle 1,4,7-trimethyl-1,4,7-triazacyclononane (L) in MeCN in the presence of air affords dark brown-black crystals of the asymmetric dinuclear species $[\text{Mn}_2\text{L}(\mu\text{-O})_2(\mu\text{-MeCO}_2)(\text{MeCO}_2)_2]$ **1** in good yields. Reaction of Christou's⁶ tetranuclear complex $\{[\text{Mn}_4\text{O}_2(\text{MeCO}_2)_7(\text{bpy})_2](\text{ClO}_4)\}$ (bpy = 2,2'-bipyridyl) and LMnCl_3 ⁷ (1:2) in water in the presence of air yields black crystals of $\{[\text{Mn}_2\text{L}(\mu\text{-O})_2(\mu\text{-MeCO}_2)(\text{bpy})(\text{H}_2\text{O})](\text{ClO}_4)_2\}$ **2a**. Recrystallisation of this species from MeOH solution results in a displacement of bound water by MeOH and black crystals of $[\text{Mn}_2\text{L}(\mu\text{-O})_2(\mu\text{-MeCO}_2)(\text{bpy})(\text{MeOH})](\text{ClO}_4)_2$ **2b** are obtained.[†]

The asymmetric complexes **1**, **2a** and **2b** contain the $[\text{Mn}^{\text{III}}(\mu\text{-O})_2(\mu\text{-MeCO}_2)\text{Mn}^{\text{IV}}]^{2+}$ core as has been established by single crystal X-ray crystallography of **1** (Fig. 1) and **2b** (Fig. 2).[‡] Three symmetrical species of this type have been characterized previously.⁸ The valences in all these cases are clearly localized. The macrocycle L stabilizes Mn^{IV} in **1** and **2b** as is judged from the shorter Mn-O_{oxo} and Mn-O_{acetate} distances of the $\text{LMn}^{\text{IV}}\text{O}_3$ fragment as compared with the corresponding Mn-O bonds of the second Mn^{III} ion. The structure of **1** is interesting because it exhibits three different carboxylate binding modes;⁹ a *syn*, *syn* bidentate bridging

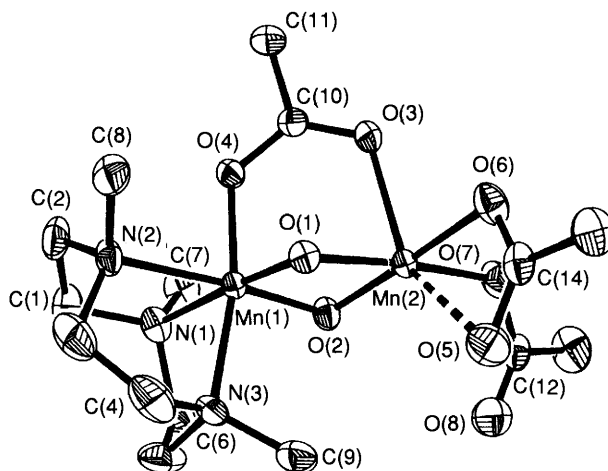


Fig. 1 Selected bond lengths (Å) and angles (°) for $[\text{Mn}_2\text{L}(\mu\text{-O})_2(\mu\text{-MeCO}_2)(\text{MeCO}_2)_2]$ **1**: Mn(1)···Mn(2) 2.665(1), Mn(1)-O(1) 1.788(4), Mn(1)-O(2) 1.767(4), Mn(1)-N(1) 2.143(6), Mn(1)-N(2) 2.131(6), Mn(1)-N(3) 2.074(4), Mn(1)-O(4) 1.945(3), Mn(2)-O(1) 1.882(4), Mn(2)-O(2) 1.864(4), Mn(2)-O(3) 2.268(4), Mn(2)-O(5) 2.654(6), Mn(2)-O(6) 1.996(5), Mn(2)-O(7) 1.944(5), Mn(2)···O(8) 3.069(6); Mn(1)-O(1)-Mn(2) 93.1(2), Mn(1)-O(2)-Mn(2) 94.4(2), O(1)-Mn(1)-O(2) 87.6(2), O(1)-Mn(2)-O(2) 82.1(2)

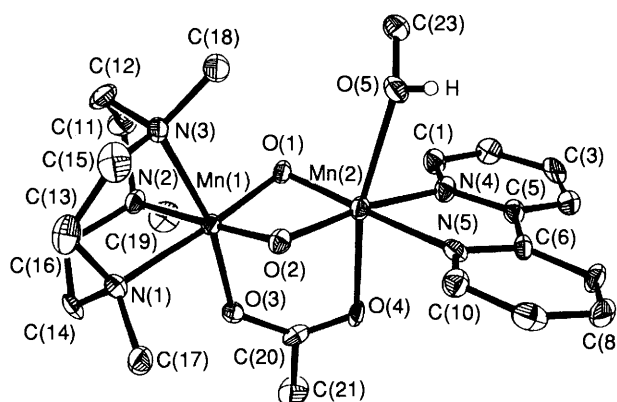


Fig. 2 Selected bond lengths (Å) and angles (°) for $[\text{MnL}(\mu\text{-O})_2(\mu\text{-MeCO}_2)\text{Mn}(\text{bpy})(\text{MeOH})]^{2+}$ **2b**: Mn(1)···Mn(2) 2.630(2), Mn(1)-N(1) 2.113(5), Mn(1)-N(2) 2.103(5), Mn(1)-N(3) 2.079(6), Mn(1)-O(1) 1.792(4), Mn(1)-O(2) 1.787(4), Mn(1)-O(3) 1.926(4), Mn(2)-N(4) 2.089(5), Mn(2)-N(5) 2.071(4), Mn(2)-O(1) 1.838(4), Mn(2)-O(2) 1.842(4), Mn(2)-O(4) 2.244(5), Mn(2)-O(5) 2.279(5); Mn(1)-O(1)-Mn(2) 92.9(2), Mn(1)-O(2)-Mn(2) 92.9(2), O(1)-Mn(1)-O(2) 86.6(2), O(1)-Mn(2)-O(2) 83.6(2), Mn(2)-O(5)-C(23) 121.3(4)

[†] Typical procedures for $[\text{Mn}_2\text{L}(\mu\text{-O})_2(\mu\text{-MeCO}_2)(\text{MeCO}_2)_2]$ **1** and $\{[\text{Mn}_2\text{L}(\text{bpy})(\text{X})(\mu\text{-O})_2(\mu\text{-MeCO}_2)](\text{ClO}_4)_2\}$ (X = H₂O **2a**, MeOH **2b**): **1**: To a solution of L (0.50 g; 2.9 mmol) in acetonitrile (40 ml) was added in the presence of air at ambient temperature, $[\text{Mn}_3^{\text{III}}(\mu\text{-MeCO}_2)_6(\mu_3\text{-O})(\text{OH}_2)_3](\text{MeCO}_2)_2$ (0.58 g; 1.0 mmol). From the greenish-brown solution brown microcrystals precipitated immediately (yield: 0.80 g). Crystals suitable for X-ray crystallography of **1** were obtained from a more dilute solution (150 ml MeCN) by allowing slow diffusion of Et₂O into this solution. **2a**: An aqueous solution (50 ml) of $\{[\text{Mn}_4\text{O}_2(\text{MeCO}_2)_7(\text{bpy})_2](\text{ClO}_4)_2\}$ (0.54 g; 0.50 mmol) and LMnCl_3 (0.34 g; 1.0 mmol) was stirred at room temperature in the presence of air for 1 h. To the brownish-green solution was added NaClO_4 (0.50 g). Upon cooling to 0°C for 12 h black crystals of $\{[\text{LMn}^{\text{IV}}(\mu\text{-O})_2(\mu\text{-MeCO}_2)\text{Mn}^{\text{III}}(\text{bpy})(\text{H}_2\text{O})](\text{ClO}_4)_2\}$ **2a** were obtained. Yield: 0.62 g; 81% based on LMnCl_3 . **2a** is readily soluble in MeOH. Cooling of a MeOH solution (50 ml) of **2a** (0.50 g) to 0°C affords within 1–2 d black crystals of $[\text{LMn}^{\text{IV}}(\mu\text{-O})_2(\mu\text{-MeCO}_2)\text{Mn}^{\text{III}}(\text{bpy})(\text{MeOH})](\text{ClO}_4)_2$ **2b** suitable for X-ray crystallography. All new complexes gave satisfactory elemental analyses (C, H, N, Mn).

[‡] Crystal data: **1**: C₁₅H₃₀Mn₂N₃O₈, triclinic, space group $P\bar{1}$, $a = 8.849(2)$, $b = 8.924(2)$, $c = 13.409(3)$ Å, $\alpha = 90.85(3)$, $\beta = 90.17(3)$, $\gamma = 104.87(3)^\circ$, $V = 1023.3(4)$ Å³, $Z = 2$, $D_c = 1.591$ g cm⁻³. A Siemens P4 diffractometer, Mo-K α radiation (graphite monochromator), was used at 293 K. 5045 reflections were collected, of which 2903 unique data with $I \geq 2\sigma(I)$ were used in refinement. The structure was solved by direct methods; the hydrogen atoms are in calculated positions. Least-squares refinement converged to final agreement factors of $R = 0.059$ and $R_w = 0.058$ for 278 variables.

For **2b**: C₂₃H₃₀Cl₂Mn₂N₅O₁₄, orthorhombic, space group $Pbca$, $a = 10.247(3)$, $b = 15.146(4)$, $c = 41.98(1)$ Å, $V = 6578(3)$ Å³, $Z = 8$, $D_c = 1.596$ g cm⁻³. The same diffractometer was used as above at 168 K. 6540 reflections were collected, of which 3963 unique data with $I \geq 2.0\sigma(I)$ were used in refinement. The structure was solved by direct methods; the positions of the hydrogen atoms at the methyl, methylene and bipyridine carbon atoms were calculated; the H-atom of coordinated methanol was located in the final difference Fourier map and included in the refinement. $R = 0.059$; $R_w = 0.0645$ for 440 variables.

Atomic coordinates, bond length and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors. Issue No. 1.

acetate, a *syn* monodentate terminal and an asymmetric chelating acetate.

Powdered samples of **1** and **2a** were used for variable-temperature magnetic susceptibility measurements (82–298 K) by using the Faraday method. The magnetic data were fitted to the expression for χ_M vs. T obtained from the isotropic spin exchange Hamiltonian $H = -2JS_1 \cdot S_2$ where $S_1 = 2$ and $S_2 = 3/2$. The values of g and J obtained for **1** are 1.98 and -90 cm⁻¹ and for **2a** are 2.0 and -117 cm⁻¹. These values are in excellent agreement with those reported for symmetrical species and indicate intramolecular antiferromagnetic coupling between a Mn^{III} (d^4 high spin) and a Mn^{IV} ion yielding an $S = 1/2$ ground state. The electronic spectrum of an MeCN solution of **2a** exhibits absorption maxima at 243 nm (2.14×10^3 l mol⁻¹ cm⁻¹), 283 (2.12×10^3), 300 sh, 410 sh, 534 (410), 620 sh; **1** is only sparingly soluble in MeCN; its spectrum has not been recorded.

Solutions of **1** and **2a** ($\approx 5.9 \times 10^{-5}$ mol l⁻¹) in an aqueous acetic acid/sodium acetate buffer (0.20 mol l⁻¹; pH = 4.6) were added to aqueous solutions of H₂O₂ (1.4 mol l⁻¹) and the

evolution of gaseous dioxygen was followed manometrically as a function of time at 20 °C. For the first 3 min (\approx 1300 turnovers) the reactions were found to follow zero-order kinetics. Subsequently, deterioration of the catalysts is appreciable and after \approx 20 min the reactions come to a complete stop. From the initial rate we calculate $V_{\max} = 5.5$ for **1** and 13.2 mol H₂O₂/mol catalyst s⁻¹ for **2a**. These model catalysts are approximately five orders of magnitude less reactive than the metalloproteins from *L. plantarum* or *T. album*. This is in agreement with two other model compounds reported by Dismukes *et al.*³ and Larson and Pecoraro.⁴

Interestingly, the following dinuclear complexes do not display catalase activity; they are rapidly reduced to manganese(II) by H₂O₂ and probably dissociate to inactive monomeric species: $[\{\text{Mn}_4\text{O}_2(\text{MeCO}_2)_7(\text{bpy})_2\}(\text{ClO}_4)]$,⁶ $[\{\text{Mn}_2(\text{bpy})_4(\mu\text{-O})_2\}(\text{ClO}_4)_3]$ ¹⁰ and $[\text{Mn}_2\text{Cl}_2(\mu\text{-O})_2(\mu\text{-MeCO}_2)(\text{bpy})_2]$.^{8b} Note that the latter species contains one half of the asymmetric species **2a**, **2b**.

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