Novel Dinuclear Manganese(III) Complexes with Tridentate and Bridging Tetradentate Schiff Base Ligands: Preparation, Properties and Catalase-like Function

Toshio Nakamura, Kenshin Niwa, Manabu Fujiwara, and Takayuki Matsushita*
Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, Seta, Otsu 520-2194

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Novel dinuclear manganese(III) complexes, Mn^{III}_2(*N*-PhO-sal)$_2$(X-sal-*m*-xylylene) (X = H, 3-MeO) have been prepared by the ligand substitution reaction and characterized, where *N*-PhOH-salH and X-sal-*m*-xylyleneH$_2$ denote *N*-2-hydroxyphenyl-salicylideneamine and *N,N'*-di-substituted-salicylidene-*m*-xylylenediamine, respectively. These complexes have been found to decompose hydrogen peroxide catalytically (H_2O_2/Mn < 100), cycling their oxidation levels between Mn_2(III,III) and Mn_2(II,II) with dioxygen evolution.

Manganese ions play an important role in biological redox enzymes such as oxygen-evolving center of photosystem II (PSII OEC), superoxide dismutases (SOD), and catalases (CAT).[1] Recently, the structure and spectroscopic analysis of the Mn-catalase has suggested that the active center consists of five- and six-coordinate asymmetrical di-manganese core and is separated by ca. 3.6 Å.[2] Additionally, it is anticipated that a water molecule comprises one of ligands and bridges between two manganese ions, but is released at initial part of reaction.[2] To design manganese complexes mimicking functions of Mn-catalases on the basis of these knowledge, it has been pointed out that each manganese ion of the dinuclear complex should adopt a five-coordinate or six-coordinate geometry which has an easily substitutable site, and two manganese ions are relatively close each other for the disproportionation of H_2O_2 to O_2 and H_2O.[3] In this paper, we describe the preparation, molecular structures of novel dinuclear manganese(III) complexes and their reactivities toward H_2O_2.

A starting mononuclear manganese(III) complex, Mn^{III}(acac)(*N*-PhO-sal) **1** was obtained by the ligand substitution reaction between $Mn^{III}(acac)_3$ (1.06 g, 3 mmol) and *N*-PhOH-salH (0.64 g, 3 mmol) in methanol (MeOH, 100 ml) at 60 °C for 6 h, and recrystallized from ethanol (EtOH) as brown prismatic crystals (0.80 g, 66% yield), where acacH and *N*-PhOH-salH denote acetylacetone and *N*-2-hydroxyphenyl-salicylideneamine, respectively. This complex (1.0 g, 2.74 mmol) was allowed to react with a half-molar amount of bridging Schiff base ligands, X-sal-*m*-xylyleneH$_2$ in MeOH and recrystallized from MeOH for **2** or acetonitrile (MeCN) for **3** to give the desired dinuclear manganese(III) complexes, Mn^{III}_2(*N*-PhO-sal)$_2$(X-sal-*m*-xylylene) {X = H: **2** (0.63 g, 53% yield), 3-MeO: **3** (0.36 g, 29% yield)} as brownish black crystals, where X-sal-*m*-xylyleneH$_2$ denotes *N,N'*-di-substituted-salicylidene-*m*-xylylenediamine. These ligand substitution reactions may take place by the differences in coordination strength among the ligands: acacH, *N*-PhOH-salH and X-sal-*m*-xylyleneH$_2$. These complexes were characterized by elemental analyses and spectroscopic, magnetic susceptibility and electrochemical measurements.[4-6] Single crystals of the complexes **1** and **2** were used for X-ray crystallographic analysis.[7]

Figure 1 shows the essential part of the complex **1** where the central manganese atom adopts a six-coordinate distorted octahedral structure: The NO_3 donor set forming an equatorial plane comes from *N*-PhO-sal and acac, and the remaining axial positions are occupied by the O_2 donor set of acac and EtOH. The Mn-O distances (2.149(8) Å in acac and 2.310(8) Å in EtOH) between the manganese atom and the axial oxygen atoms are longer than the average of other three Mn-O distances (ca. 1.897 Å), which may be arisen from the Jahn-Teller effect.

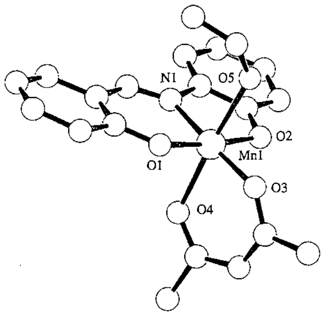

Figure 1. Molecular structure of [Mn^{III}(acac)(*N*-PhO-sal)(EtOH)] **1**·EtOH. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows: Mn1-O1 1.877(7), Mn1-O2 1.900(7); Mn1-O3 1.914(7), Mn1-O4 2.148(7), Mn1-O5 2.305(8), Mn1-N1 2.009(9), O1-Mn1-O2 174.3(3), O3-Mn1-N1 172.9(4) O4-Mn1-O5 172.3(3).

Figure 2 shows a perspective view of the complex **2**. The X-ray reflection data enough to solve the complete structure of the complex **2** could not be collected owing to quick degradation of the crystal in the air. However, the results suggested that two manganese ions in the complex are bridged by one sal-*m*-xylylene ligand and each of them has a six-coordinate structure of a N_2O_4 donor set including a coordinated MeOH molecule, which is similar to that of the mononulear complex **1**. Upon standing the crystal of the complex **2**·2MeOH, some breakage of the crystal occurred to form **2**·MeOH, which was confirmed by the elemental analysis.[5] In this complex, the manganese ion may adopt a five-coordinate structure. When the dinuclear complex **3**

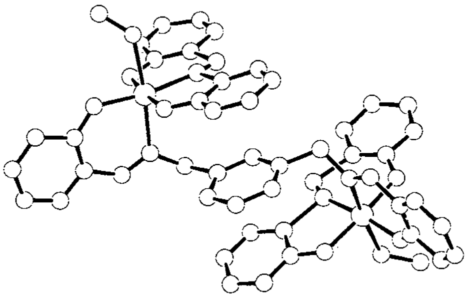

Figure 2. A perspective view of [Mn^{III}_2(*N*-PhO-sal)$_2$(sal-*m*-xylylene)(MeOH)$_2$] **2**·2MeOH.

was recrystallized from MeCN, its analytical data agreed with a composition of the formula of **3**·0.5MeCN.[6] These results indicate that each manganese ion in the present dinuclear complexes may prefer to adopt a five-coordinate structure.

The reactivities of these manganese complexes **2** and **3** toward H_2O_2 were investigated by measuring changes in the UV-vis and EPR spectra and cyclic voltammograms and a volumetric determination of the evolved dioxygen during their reactions with H_2O_2. The results indicate that the complexes **2** and **3** have been found to decompose H_2O_2 (H_2O_2/Mn < 100) catalytically without any degradation of the complexes. However, some decomposition of the complexes has been found to occur with an increase in the molar ratios of H_2O_2 to Mn = 100 and above. The reactivity of the complex **3** toward H_2O_2 in DMF has been found to be slightly more effective in decomposition rate than that of the complex **2** (see Figure 3). Moreover, the decomposition rates of H_2O_2 by the complex **3**, which is selected by its good solubility in organic solvents, have been found to depend strongly on the solvents used. As shown in Figure 3, the periods to reach vigorous evolution of dioxygen are decreased in the order of MeOH, *N*,*N*-dimethylformamide (DMF) and MeCN. The results suggest that the central manganese(III) ions in the dinuclear manganese(III) complex adopt a solvated six-coordinate structure in MeOH and/or DMF, which was confirmed by the reasonable shifts of the absorption bands in the d-d transition region and of the redox potentials for Mn(III) ⇔ Mn(II).

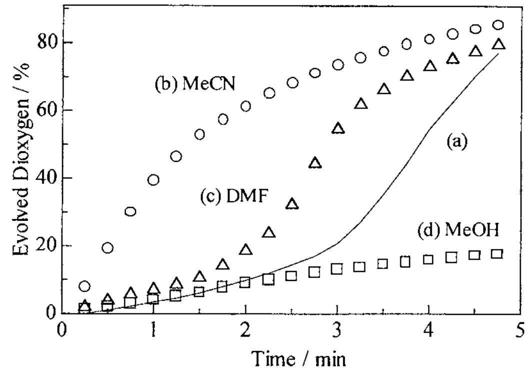

Figure 3. Time courses of oxygen evolution in the disproportionation of H_2O_2 by the complex **2** in DMF (a), and the complex **3** in MeCN (b), in DMF (c) and in MeOH (d): [complex] = 1 mM, [H_2O_2] = 100 mM, at 22 ℃.

Figure 4 shows EPR spectral changes of a MeCN solution of the complex **3** during the reaction with H_2O_2 measured at -70 ℃. The EPR spectrum of the complex **3** in MeCN shows no signal (Figure 4-a), because a manganese(III) ion is EPR silent. By the addition of a MeCN solution of H_2O_2 to it, a six-line signal appeared around g = 2.0 with a coupling constant of A_{av} = 0.0091 cm^{-1} (Figure 4-b), which can be ascribed to the formation of manganese(II) species of the complex **3** reduced by H_2O_2. By allowing to stand the solution for 60 min, the six-line signal disappeared gradually to become EPR silent again (Figure 4-c). These results indicate that the oxidation states of the dinuclear manganese(III) complex may cycle between Mn_2(III,III) and Mn_2(II,II).[3]

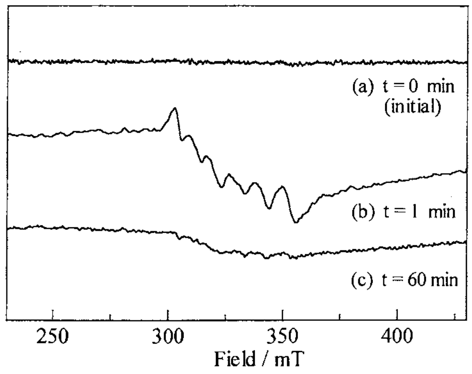

Figure 4. EPR spectra during the reaction of the complex **3** with H_2O_2 in MeCN: T = -70 ℃, power = 5.00 mW, [**3**] and [H_2O_2] = 1 mM. (b) An averaged coupling constant(A_{av}) is 0.0091 cm^{-1}.

In conclusion, we have found that the designed dinuclear manganese(III) complexes can be obtained by step-wise ligand substitution reaction. The reactivities of other dinuclear manganese(III) complexes toward H_2O_2 and the detailed mechanism are now in progress.

References and Notes

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4 Physicochemical data for **1**: UV-visible spectra (DMF): λ_{max} = 454 nm (logε = 3.89). Cyclic voltammogram (DMF): $E_{1/2}$ = 0.12 V (III⇔II)(vs. SCE). Magnetic moment per Mn: 5.00 μ_B (297 K). Anal. Found: C, 58.47; H, 5.44; N, 3.53; Mn, 13.00%. Calcd for **1**·EtOH, $C_{20}H_{22}NO_5Mn$: C, 58.40; H, 5.39; N, 3.41; Mn, 13.36%.

5 Physicochemical data for **2**: UV-visible spectra (DMF): λ_{max} = 466 nm (logε = 4.10). Cyclic voltammogram (DMF): $E_{1/2}$ = -0.42 V (III⇔II), 0.74 V (IV⇔III)(vs. SCE). Magnetic moment per Mn: 4.79 μ_B (297 K). Anal. Found: C, 64.70; H, 4.33; N, 6.09; Mn, 12.01%. Calcd for **2**·MeOH, $C_{49}H_{40}N_4O_7Mn_2$: C, 64.90; H, 4.45; N, 6.18; Mn, 12.12%.

6 Physicochemical data for **3**: UV-visible spectra (DMF): λ_{max} = 466 nm (logε = 4.09). Cyclic voltammogram (DMF): $E_{1/2}$ = -0.48 V (III⇔II), 0.67 V (IV⇔III)(vs. SCE). Magnetic moment per Mn: 4.88 μ_B (297 K). Anal. Found: C, 63.92; H, 4.52; N, 6.68; Mn, 11.32%. Calcd for **3**·0.5MeCN, $C_{51}H_{41.5}N_{4.5}O_8Mn_2$: C, 64.12; H, 4.38; N, 6.60; Mn, 11.50%.

7 Crystal data for **1**·EtOH: formula = $C_{20}H_{22}MnNO_5$, F_W = 411.34, monoclinic, space group $P2_1/a$, a = 11.455(4), b = 20.308(6), c = 8.441(4)Å, β = 90.36(3)°, Z = 4, V = 1963(1) $Å^3$, d_{calcd} = 1.391 g/cm^3, μ(Mo-Kα) = 7.02 cm^{-1}, T = 296 K, R (R_W) = 0.050 (0.065) for 1077[I > 3.00$\sigma(I)$] reflections.