Dimanganese Complexes Bridged with a (μ-X)(μ-Carboxylato) Unit as Models for the Active Site of Manganese Catalase (X=OH, O or $(O)_2$)

Masahisa Osawa, Kiyoshi Fujisawa, Nobumasa Kitajima, and Yoshihiko Moro-oka*
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226

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A novel dimanganese complex $LMn^{II}(OH)(OAc)Mn^{II}L$ (**1**) (L = hydrotris(3,5-diisopropyl-1-pyrazolyl)borate) was synthesized by the reaction of $LMn^{II}(OH)_2Mn^{II}L$ with 1 equiv of acetic acid. Complex **1** was oxidized either by dioxygen or anaerobic reaction with H_2O_2, resulting in the formation of two isolable products $[LMn^{III}(O)(OAc)Mn^{III}L]^+$(**2**) and $LMn^{III}(O)_2(OAc)Mn^{IV}L$ (**3**). The formation of **2** was identified by comparison with an authentic sample prepared from bis(μ-oxo) complex $LMn^{III}(O)_2Mn^{III}L$. The structure of the **3** was determined by X-ray crystallography.

Dinuclear Mn complexes containing carboxylato bridges have attracted much attention in recent years because of its potential biological relevance.[1] In addition to the teteranuclear Mn site in OEC,[2] dinuclear Mn sites have been found in several non-heme catalases[3] and in ribonucleotide reductase.[4] Whereas the structural details remain unclear, both enzymes are suggested to function with a Mn(II,II)/(III,III) redox couple; a mixed valence state Mn(III,IV) or Mn(II,III) is also known for catalases as a catalytic inactive met-form.[3] On the basis of the X-ray structure of non-heme iron ribonucleotide reductase[5] and the close resemblance in optical spectra of the Mn(III,III) state of these proteins to those of Mn(III,III) complexes having a (μ-oxo)bis(μ-carboxylato) bridge,[6] the dinuclear site in Mn catalase or ribonucleotide reductase has been suggested to possess a bridging unit comprised of oxo(or hydroxo) and carboxylato groups.[1, 6] While several dinuclear Mn complexes having a (μ-oxo)bis(μ-carboxylato)[6] or a (μ-hydroxo)bis(μ-carboxylato)[7] bridge are known, there is no example of the corresponding complexes bridged with a single carboxylato unit. As part of our synthetic exploration of dinuclear Mn complexes with a hindered tris(pyrazolyl)borate ligand (L = hydrotris(3,5-diisopropyl-1-pyrazolyl)borate),[8] we now report dinuclear complexes bridged with a single carboxylato unit.

In a similar manner applied to the synthesis of a (μ-hydroxo)(μ-carboxylato) Fe^{II} complex,[9] the anaerobic reaction of a bis(μ-hydroxo) complex $LMn^{II}(OH)_2Mn^{II}L$ (**4**)[8a] with 1 equiv of acetic acid gave a novel dinuclear complex, $LMn^{II}(OH)(OAc)Mn^{II}L$ (**1**).[10] Although we have not yet succeeded in determining the crystal structure, the analytical data, FDMS (field desorption mass spectroscopy) and some other spectroscopic data are all consistent with this structure.[10]

When complex **1** was treated in toluene either with dioxygen or with hydrogen peroxide under argon, pronounced color change of the solution from pale yellow to dark brown was noted. From the resulting solution, two brown colored products were isolated by fractional recrystallizations from acetonitrile. The FDMS analyses indicated that these complexes are formulated as $[LMn^{III}(O)(OAc)Mn^{III}L]^+$ (**2**) and $LMn^{III}(O)_2(OAc)Mn^{IV}L$ (**3**), respectively.[11] Support for these structures was further provided from the analytical and spectroscopic data, particularly by EPR. Whereas **2** is EPR silent at -160 ℃, **3** gives a 16-line signal typical for a mixed valence Mn(III,IV) complex of which each Mn ion adopts a six-coordinate structure.[1]

The X-ray structure of **3** was determined and the ORTEP view is presented in Figure 1.[12] The Mn-O distances of 1.82 and 1.79 Å are typical for a bis(μ-oxo) moiety. Several X-ray structures of similar Mn(III,IV) complexes containing a bis(μ-oxo)(μ-carboxylato) bridge have been reported.[1, 13] The Mn•••Mn separation in these complexes (2.59 - 2.67 Å) were pointed out to be longer than those of Mn(III,IV) complexes (2.7 Å) bridged with a bis(μ-oxo) unit.[3] The Mn•••Mn separation found in **3** (2.709 Å), however, falls in the range of the later type complexes; this presumably reflects the highly steric bulk of the tris(pyrazolyl)borate ligand. Although all the Mn(III,IV) complexes are asymmetric, the molecule of **3** sits on a crystallographically imposed C_2 axis and thus has a symmetric structure. This is controversial because the 16-line EPR signal is not expected for such a symmetric structure. We infer this due to the serious crystallographic disorder but more investigations are necessary to address this unusual feature. Lippard et al. reported a closely related complex to **3** with hydrotris(1-pyrazolyl)borate $HBPz_3$ which was chemically generated from $(HBPz_3)Mn^{III}(O)(OAc)_2Mn^{III}(HBPz_3)$, though this mixed valence complex was not crystallized.[6b]

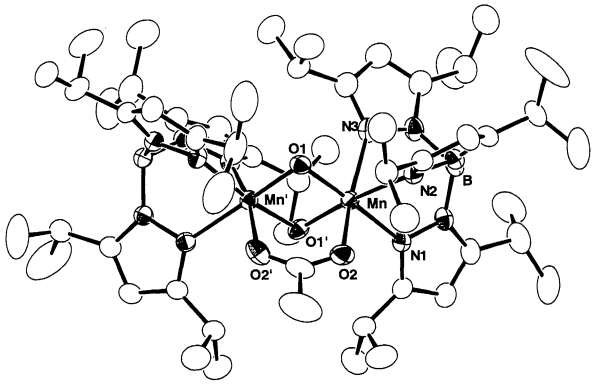

Figure 1. ORTEP view of $LMn^{III}(O)_2(OAc)Mn^{IV}L$ (**3**). Selected bond distances (Å) and angles (deg) are as follows. Mn-N1, 2.089 (3); Mn-N2, 2.122 (2); Mn-N3, 2.230 (3); Mn-O1, 1.821 (2); Mn-O1', 1.794 (2), Mn-O2, 2.079 (2); Mn•••Mn', 2.709 (1); Mn-O-Mn', 96.8 (1).

The authentic complex of **2** was prepared as a BF_4^- salt by the reaction of a bis(μ-oxo) complex $LMn^{III}(O)_2Mn^{III}L$ with 1 equiv of HBF_4 and acetic acid.[14] The formation of **2** from **1** was established by the comparison with the authentic **2**•BF_4. The optical spectrum of **2** exhibits broad shoulder band at ca. 480 nm which resembles those of manganese catalases[3] and ribonucletotide reductase.[4]

In order to shed light on the reaction mechanism, labeling experiment of the aerobic oxidative conversion of **1** into **3** was carried out. The FDMS spectroscopy indicated that solely ^{18}O incorporated **3** is formed when ^{16}O labeled **1** was treated with $^{18}O_2$. Conversely, when ^{18}O labeled **1** was oxidized under $^{16}O_2$, only ^{16}O incorporated **3** was yielded. These results establish that the bis(μ-oxo) unit originates from the externally added dioxygen but not from the hydroxo group in **1**. When a 1:1 mixture of $^{18}O_2$ and $^{16}O_2$ was employed to oxidize ^{16}O labeled **1**, the products formed was a 1:1 mixture of **3** containing two ^{16}O or ^{18}O, respectively; no mixed labeled product was produced. This provides evidence that both oxygen atoms in the bis(μ-oxo) bridging unit come from the same molecule of dioxygen. Based on these observations, we propose the mechanism of the oxidative formation of **3** as illustrated in Figure 2. The key reaction step is the formation of μ-peroxo Mn(III,III) complex followed by the O-O bond homolysis with the electoron delocalization. A similar reaction mechanism was proposed previously for ligand hydroxylation in $LMn^{II}(OH)_2Mn^{II}L$ with dioxygen.[8b]

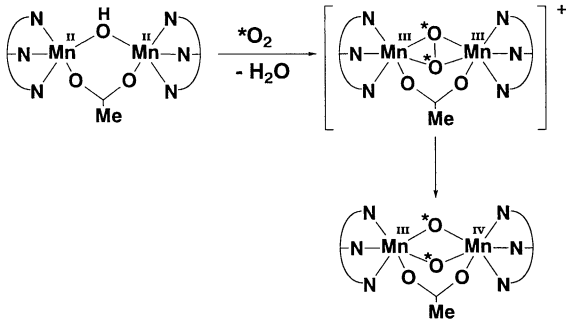

Figure 2. The proposed mechamism for the oxidation of $LMn^{II}(OH)(OAc)Mn^{II}L$ (**1**).

While many aspects of structure and property remain to be elucidated, the preliminary chemistry of the (μ-carboxylato) dinuclear Mn complexes **1-3** parallels that known for manganese catalases, lending support to the hypothetical model proposed by Dismukes; [15-16]the two manganese ions are bridged with a single carboxylato unit as in **1-3** in their respective oxidation state.

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10 Recrystallization from CH_2Cl_2 gave **1** solvated with CH_2Cl_2 as colorless crystals. Satisfactory elemental analysis was obtained for **1** dried under vacuum. Anal. Calcd for $C_{55}H_{96}N_{12}O_3B_2Mn_2$: C, 60.23; H, 8.66; N, 15.05. Found: C, 60.42; H, 8.34; N, 14.79. IR (KBr, cm^{-1}): ν(OH), 3652; ν (BH), 2541; ν(COO), 1573; ν (COO), 1428. FDMS (m/e): 1117. μ_{eff}: 7.41 μ_B/mol at 295 K.

11 Complex **2** which is more soluble in acetonitrile than **3** was obtained as brown powders in ca. 38% yield from **1**, the structural identification being accomplished by comparison with the authentic sample.[14] Complex **3** was isolated as dark brown crystals suitable for X-ray diffractions in ca. 20% yield by recrystallization from acetonitrile. Calcd for $C_{56}H_{95}N_{12}O_4B_2Mn_2$: C, 59.42; H, 8.46; N, 14.85. Found: C, 59.13; H, 8.65; N, 14.88. IR (KBr, cm^{-1}): ν (BH), 2543; ν (COO), 1574; ν (COO), 1428. UV-vis (nm, $\varepsilon/cm^{-1}M^{-1}$): 720 (170). μ_{eff}: 2.69 μ_B at 295 K.

12 **3** (fw 1131.94) crystallized in the monoclinic space group *C2/c* with a = 29.142(6) Å, b = 11.793(2) Å, c = 21.290(5) Å, β = 117.77(1)°, V = 6475(6) Å^3, and Z = 4. The structure was determined by the direct method (MITHRIL) and refined based on 4046 reflections with $F_o \geq 3\sigma(F_o)$ ($5° \geq 2\theta \geq 50°$), collected at 298 K. The current R (R_w) factor is 4.02 (5.06)%.

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14 In a 20 mL of ether, $LMn^{III}(O)_2Mn^{III}L$ (0.445g, 0.42 mmol) was reacted with an equimolar amount of tetrafluoroboric acid and acetic acid for 30 min at -78 °C. The solution was dried under vacuum and the resulting solid was recrystallized from acetonitrile, affording **2**•BF_4 as reddish brown solid (0.26 g, 0.22 mmol, 52% yield). Calcd for $C_{56}H_{95}N_{12}F_4O_3B_3Mn_2$: C, 55.92; H, 7.90; N, 14.05. Found: C, 55.66; H, 8.33; N, 14.22. IR (KBr, cm^{-1}): ν(BH), 2543; ν(COO), 1570; ν(COO), 1433. FDMS (m/e): 1116(**2**, 88%), 1203(**2**+BF_4, 12%). μ_{eff}: 3.25 μ_B/mol at 295 K.

15 The Mn(II,II) and Mn(III,III) states of Mn catalase are effective for disproportionation of hydrogen peroxide, whereas the Mn(III,IV) state is inactive. As consistent, complexes **1** and **2** exhibit the catalase activity in toluene at room temperature, but **3** is completely inactive.

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