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Dinuclear Manganese(II) Complexes with Water and Carboxylate Bridges

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Several metalloproteins require manganese to perform their biological functions and have recently become important targets for synthetic modeling studies.[1-13] Dinuclear manganese centers have been found in *Lactobacillus plantarum* pseudocatalase, which catalytically disproportionates H_2O_2,[14-16]and in the small subunit of *Brevibacterium ammoniagenes* and *Micrococcus luteus* ribonucleotide reductase (RR), which facilitates the reduction of ribonucleotides to deoxyribonucleotides[17-19] A tetranuclear manganese center has been proposed as the active site in the oxygen evolving center (OEC) of photosystem II (PSII), where H_2O is oxidized to O_2.[20-26] X-ray analyses performed on pseudocatalase from *Thermus thermophilus* revealed that the distance between the two manganese atoms is 3.6 Å,[27] and an EPR investigation showed that the dinuclear center could achieve three oxidation states, $Mn^{II}Mn^{II}$, $Mn^{II}Mn^{III}$, and $Mn^{III}Mn^{IV}$.[16] Studies on the native manganese containing RR indicated it may possess the same structure type as its well-studied iron RR counterpart,[19] and X-ray crystallographic investigations of the Mn(II)-reconstituted B2 subunit from *E. coli* (RRB2) have recently revealed the presence of two Mn(II) ions at a distance of 3.6 Å connected by two bridging carboxylate ligands; a water molecule is coordinated to one of the Mn(II) atoms.[28] Although X-ray crystallographic information is not available for the OEC in PSII, EPR[23] and EXAFS[21,24-26] studies indicated the presence of four manganese atoms in the active center, with two of them separated by 2.7 Å and possibly a third located 3.3 Å from its nearest metal neighbor. Oxygen atoms from amino acid carboxylate groups comprise the majority of the first coordination sphere at these manganese atoms. The remaining donors are probably nitrogen atoms from histidine residues. Recently, we have been exploring the chemistry of polynuclear manganese(II) carboxylate complexes to mimic features of these biological centers. In this communication, we report the preparation, structural characterization, and magnetic properties of two (μ-aqua)-bis(μ-carboxylato)dimanganese(II) complexes, $[Mn_2(H_2O)(piv)_4(Me_2bpy)_2]$ (**1**) and $[Mn_2(H_2O)(OAc)_4(tmeda)_2]$ (**2**). They are rare examples of water-bridged dinuclear Mn(II) complexes,[29] have properties similar to those of the dimanganese centers in some of the proteins, and serve as useful precursors to higher nuclearity clusters.

To a suspension of 0.51 g (2.0 mmol) of $Mn(piv)_2$[30,31] in 30 mL of MeOH was added 0.39 g (2.10 mmol) of solid 4,4′-Me_2-bpy. The reaction mixture was stirred for 2 h and then filtered. From this yellow filtrate, which was kept in an open flask at room temperature, were obtained yellow crystals of **1** suitable for X-ray diffraction studies.[32] Two portions of THF (20 mL) were used to wash out the free ligand which cocrystallized from the filtrate. The yield for the analytically pure product was 0.41 g (45%). This material was also analyzed for elemental composition

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(30) Abbreviations: piv, pivalate; Me_2bpy, 4,4′-dimethyl-2,2′-bipyridine; OAc, acetate; tmeda, *N,N,N′,N′*-tetramethylethylenediamine.
(31) $Mn(piv)_2$ was prepared by refluxing $MnCO_3$ with excess pivalic acid in H_2O overnight. The supernatant was decanted and the resulting pink oil washed with H_2O and allowed to stand at room temperature to afford the product as a pinkish solid. C and H analyses confirm the formula of $Mn(piv)_2$.
(32) Crystallographic data for **1** ($C_{44}H_{62}Mn_2N_4O_9$, fw 900.87) and, in parentheses, **2** ($C_{20}H_{46}Mn_2N_4O_9$, fw 596.48) at 193 K: triclinic (orthorhombic), space group $P\bar{1}$ (*Pbca*); a = 14.269 (2) (15.802 (6)) Å, b = 15.876 (3) (31.46 (1)) Å, c = 11.134 (1) (12.136 (3)) Å, α = 97.93 (1)°, β = 107.34 (1)°, γ = 76.44 (1)°, V = 2334 (1) (6034 (6)) $Å^3$, Z = 2 (8), ρ_{calc} = 1.282 (1.313) g cm^{-3}. With the use of 6230 (2419) unique reflections ($F_o > 3\sigma(F_o)$) collected with Mo Kα (λ = 0.710 69 Å) radiation between $3° < 2\theta < 54°$ on an Enraf-Nonius CAD-4 X-ray diffractometer, the structures were solved by direct methods (MITHRIL) and Fourier techniques and refined by least squares using 538 (322) variables to R = 0.048 (0.051) and R_w = 0.059 (0.055). All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms of the H_2O molecules (H1, H2) were refined with fixed isotropic thermal parameters.

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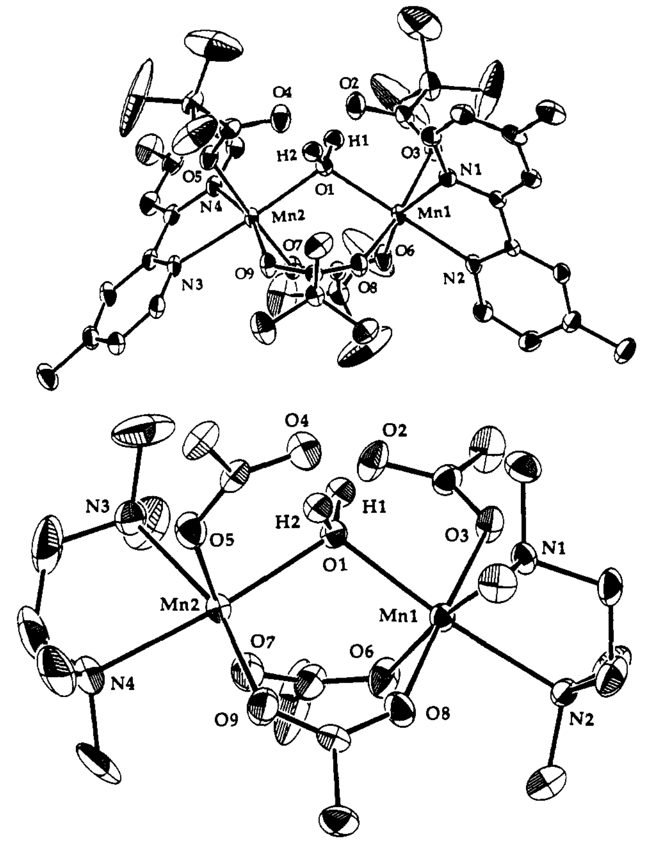

Figure 1. ORTEP drawings of **1** (top) and **2** (bottom), showing 35% probability thermal ellipsoids and atom labels for the manganese, oxygen, and nitrogen atoms. Important interatomic distances (Å) and angles (deg) of **1** and **2** (in parentheses) are as follows: Mn1–O1 = 2.182 (3) (2.215 (5)), Mn2–O1 = 2.203 (3) (2.205 (5)), Mn1–O3 = 2.297 (3) (2.174 (5)), Mn1–O6 = 2.100 (3) (2.138 (5)), Mn1–O8 = 2.150 (3) (2.124 (5)), Mn2–O5 = 2.202 (3) (2.151 (5)), Mn2–O7 = 2.177 (3) (2.129 (5)), Mn2–O9 = 2.115 (3) (2.134 (6)), Mn1–N1 = 2.282 (3) (2.340 (6)), Mn1–N2 = 2.252 (3) (2.316 (6)), Mn2–N3 = 2.264 (3) (2.424 (7)), Mn2–N4 = 2.287 (3) (2.318 (7)), O1–H1 = 0.94 (4) (1.04 (6)), O1–H2 = 0.90 (4) (0.85 (6)), O1···O2 = 2.498 (4) (2.557 (7)), O1···O4 = 2.539 (4) (2.554 (7)); Mn1–O1–Mn2 = 110.2 (1) (110.0 (2)), H1–O1–H2 = 112 (3) (109 (5)), O2···O1···O4 = 115.2 (1) (121.4 (3)).

and by FT-IR, UV-vis, and magnetic measurements.[33] Compound **2** was obtained by dropwise addition of 0.62 mL (0.41 mmol) of tmeda to a solution of 1.0 g (0.41 mmol) of $Mn(OAc)_2 \cdot 4H_2O$ dissolved in 50 mL of MeOH under Ar. The mixture was stirred for 10 min, the solvent removed in vacuo, and the residue extracted with 30 mL of hexane. This solution was allowed to stand at −20 °C for 12 h, affording colorless crystals of the product in a yield of 0.54 g (44%). These crystals proved to be suitable for X-ray diffraction studies and other physical measurements.[32,34]

The molecular structures of **1** and **2** are presented in Figure 1. Both contain a core of two Mn(II) atoms bridged by a water molecule and two bidentate carboxylate ligands. One additional monodentate carboxylate ligand is coordinated to each of the Mn atoms. The noncoordinating oxygen atoms on these two carboxylates are strongly hydrogen bonded to the bridging water molecule, as indicated by the short O1···O2 and O1···O4 distances. As a consequence, the O–H stretching frequency is dramatically shifted to ~1965 cm^{-1}. Two N atoms from the terminal bidentate nitrogen donor ligands complete the coordination sphere around each manganous ion. This structural arrangement has been observed for several other divalent metal ions, namely, Ni^{2+},[35,36] Co^{2+},[37,38] Ru^{2+},[39–41] and Fe^{2+}.[42] The distances between the two Mn atoms in **1**, 3.5950 (9) Å, and **2**, 3.621 (2) Å, are almost identical to the distance between two manganese atoms in the catalase and in the manganese reconstituted RR. They are, however, shorter than the Mn···Mn separation of 3.739 (2) Å in $[Mn_2(H_2O)_3(F_5C_2CO_2)_4(L)_2]$ (**3**), which is the only other known water-bridged dimanganese(II) complex.[29] The coordination sphere of the manganese atoms in **3**, however, differs from that of **1** and **2** because it contains only oxygen atoms. The Mn···Mn distances in these (μ-aqua)bis(μ-carboxylato)dimanganese(II) complexes are shorter than the distance in one tris(μ-carboxylato)dimanganese(II) complex, 4.034 (2) Å,[43] and one bis(μ-carboxylato) complex, 4.298 Å,[44] but longer than the Mn···Mn distance in the (μ-hydroxo)bis(μ-carboxylato) complex, 3.351 (3) Å.[45]

Variable-temperature (2–300 K) magnetic susceptibility measurements for polycrystalline solids of **1** and **2** revealed a reduction in effective moments with decreasing temperature from 7.769 to 0.914 μ_B/molecule for **1** and from 8.020 to 0.671 μ_B/molecule for **2**, indicative of antiferromagnetic coupling between two Mn(II) ions. A least-squares fit of the molar susceptibilities by using the general isotropic exchange Hamiltonian, $\mathcal{H} = -2J(S_1 \cdot S_2)$, $S_1 = S_2 = {}^5/_2$, produced $J = -2.73$ (2) cm^{-1}, $g = 1.939$ (3), $\Theta = 0.43$ (8), and $P = 0.8$ (1) (P is the percent $S = {}^5/_2$ paramagnetic impurity) for **1**, and $J = -2.952$ (7) cm^{-1}, $g = 2.012$ (1), $\Theta = 0$, and $P = 0.38$ (1) for **2**. These small negative exchange coupling constants are consistent with the long distances between the two manganese ions and agree well with the notion that antiferromagnetic coupling between two metal ions depends on the bridging ligands with $|J|$ values following the order $O^{2-} > OH^- > H_2O$.[29] They are slightly larger than the coupling constant of **3** ($J = -1.65$ cm^{-1}),[29] which can be explained by its longer Mn···Mn distance.

Complexes **1** and **2** are susceptible to atmospheric oxidation in both protic and nonprotic solvents. One very interesting product, a red crystalline material, arose from the slow air oxidation of **1** at room temperature in MeOH. X-ray crystallographic analysis revealed it to be the tetranuclear manganese complex $[Mn_4O_2(piv)_7(Me_2bpy)_2]^+$, the butterfly-type arrangement of which is known.[46,47] A hexanuclear manganese complex, $[Mn_6O_2(piv)_{10}(THF)_4]$, which was also crystallographically characterized, was obtained from the air oxidation of **1** in THF. This result suggests that a water-bridged dinuclear manganese complex could be an intermediate in the formation of higher nuclearity manganese complexes, including some that have been proposed as possible models for the active site in PSII. Char-

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(33) Analytical data for **1**: C, H, N analyses; FT-IR (KBr, cm^{-1}) 1970 (ν_s, OH), 1621, 1581 (ν_{as}, OCO), 1412 (ν_s, OCO); electronic spectrum (MeOH) featureless between 340 and 800 nm. The samples for susceptibility studies were ground and dried under vacuum before measurements were made.

(34) Analytical data for **2**: C, H, N, analyses; FT-IR (KBr, cm^{-1}) 1960 (ν_s, OH), 1608, 1575 (ν_{as}, OCO), 1413 (ν_s, OCO); electronic spectrum (MeOH) featureless between 340 and 800 nm.

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acterization of other products as well as kinetic studies for these oxidation reactions are in progress.

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Supplementary Material Available: Tables S1 and S2, reporting atomic positional and equivalent isotropic thermal parameters for **1** and **2**, and Figures S1 and S2, depicting the observed and calculated χ vs T curves for the two complexes (7 pages). Ordering information is given on any current masthead page.