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Oxidative Charge Storage on an Oxomanganese(IV) Dimer Containing a Bis(μ-oxo)–Mono(μ-Carboxylato) Bridge and Two Coordinated Water Molecules: $[Mn_2O_2(O_2CCH_3)(H_2O)_2(bpy)_2](ClO_4)_3$[1]

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A multitude of enzymes containing oxo-bridged manganese sites have recently been isolated.[2] Prominent among these are the enzymes involved in redox transformations of dioxygen precursors, i.e. the two electron oxidation of peroxide to dioxygen in dimanganese catalases[3,4] and the four-electron oxidation of water to dioxygen in the oxygen evolving center (OEC) of photosystem II (PSII).[5] The OEC achieves oxidation of water by four sequential oxidative steps (S_0–S_4),[6] involving essentially metal centered oxidations. A crucial feature of the S_0–S_4 mechanism is the fact that H_2O oxidation apparently does not occur prior to reaching the [S_4] state,[7] which suggests a stabilization of the Mn–aquo bond during oxidative charge buildup on the OEC. A cluster containing four Mn ions imbedded in a "dimer of bis(μ-oxo) dimer" type structure with a short Mn–Mn distance of ~2.7 Å and a longer Mn–Mn distance of ~3.3 Å is thought to describe the OEC in PSII.[8]

We report here the synthesis and structural characterization of the dinuclear complex $[Mn_2O_2(O_2CCH_3)(H_2O)_2(bpy)_2]^{3+}$ (**1**) containing a novel bis(μ-oxo)mono(μ-carboxylato)dimanganese(IV,IV) unit with a terminally bound water molecule on each Mn(IV). Although many dinuclear oxo–Mn(IV) cores have previously been assembled in both aqueous and non-aqueous media,[2b,9] complex **1** is the first example of a Mn(IV,IV) dimer that has coordinated biologically relevant aquo and carboxylato lignads in one molecule. It was synthesized by the *in situ* oxidation with perchloric acid of the Mn(III,III) dimer, $[Mn_2O(O_2CCH_3)_2(H_2O)_2(bpy)_2]^{2+}$ (**2**),[10] which possesses the prevalent μ-oxobis(μ-carboxylato) structural motif. Thus to 20 mL of methanol containing 0.490 g (2.0 mmol) of $Mn(O_2CCH_3)_2{\cdot}4H_2O$ was added 3 mL of glacial acetic acid followed by 0.390 g (2.5 mmol) of bpy to give a yellow solution. Addition to this mixture of 0.079 g (0.5 mmol) of $KMnO_4$ in 5 mL of water generated a red-brown solution containing **2**, which was stirred for 5 min. Treatment of this solution with 4 mL of 70% aqueous $HClO_4$ gave a dark green-brown solution which upon standing undisturbed for 2 days at room temperature yielded X-ray quality black crystals of **1**.[11] Elemental analysis[12] and single crystal diffraction data[13] indicated the formula, $Mn_2O_2(CH_3CO_2)(H_2O)_2(bpy)_2{\cdot}3HClO_4{\cdot}H_2O$.

Caution! *Perchloric acid and its salts are all potentially explosive and should be handled with care.*

The balanced reaction shown in eq 1 predicts a maximum yield of 50% for **1**, while we observe an approximately 40% yield.[14]

$$2Mn^{III}{}_2(O)(OAc)_2(H_2O)_2 + 3H^+ \rightarrow Mn^{IV}{}_2(O)_2(OAc)(H_2O)_2 + 2Mn^{II}(H_2O) + 3AcOH \quad (1)$$

The crystal structure of **1**, which is shown in Figure 1, proves the molecule contains the $\{Mn_2O_2(O_2CR)\}^{3+}$ core with each Mn(IV) terminally coordinated to an aquo molecule and the bpy ligand completing the distorted octahedral geometry. Previously, the one-electron richer $\{Mn_2O_2(O_2CR)\}^{2+}$ core has been structurally characterized in a number of Mn(III,IV) dimers, with ligands such as bpy,[15] tpen,[16] tacn,[17] and $HB(pz)_3^-$,[18,19] by X-ray crystallography[15–18] and resonance Raman spectroscopy.[19] Typically the propensity of Mn(IV), a hard acid, to bind to hard bases leads to the replacement of the acetate groups by additional oxo bridges which stabilize the higher oxidation state. This is supported by the fact that at the (IV,IV) oxidation level, there are several tribridged dimers isolated: a tris(μ-oxo)-bridged $[Mn_2O_3(Me_3tacn)_2]$,[9] a bis(μ-oxo)–μ-peroxo-bridged $[Mn_2O_2(\mu\text{-}O_2)(Me_3tacn)_2]$,[20] a bis($\mu$-oxo)–$\mu$-phosphato-bridged $[Mn_2O_2(\mu\text{-}HPO_4)(H_2PO_4)_2(bpy)_2]$,[21] and the bis($\mu$-oxo)–$\mu$-acetato-bridged

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(1) Abbreviations used: bpy, 2,2′-bipyridine; phen, 1,10-phenanthroline; tpen, *N,N,N′,N′*-tetrakis(2-pyridylmethyl)-1,3-ethanediamine; bpea = *N,N*,-bis(2-pyridylmethyl)ethylamine; tacn, 1,4,7-triazacyclononane; Me_3tacn, *N,N′,N″*-trimethyl-1,4,7-triazacyclononane; $HB(pz)_3^-$, hydrotris(1-pyrazolyl)borate.

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(11) The preparation of **1** was also achieved by dissolving a preisolated dimer **2** in CH_3OH/CH_3COOH solution, followed by acidification with $HClO_4$.

(12) Anal. Calcd for $C_{22}H_{23}Cl_3N_4O_{19}Mn_2$: C, 30.56; H, 2.87; N, 6.48; Mn 12.73. Found: C, 29.31; H, 2.75; N, 6.52; Mn 12.80.

(13) Crystal data: $C_{22}H_{23}Cl_3Mn_2N_2O_{19}$; monoclinic space group $P2_1/n$, a = 13.649(3) Å, b = 16.230(3) Å, c = 16.284(3) Å, β = 113.10(3)°, V = 3318.1(11) Å^3, Z = 4, R = 5.40, and R_w = 6.34 for 3231 observed ($F > 4.0\sigma(F)$) reflections. Diffractometer data (Mo Kα radiation) were collected in the range $3.5 \leq 2\theta \leq 45°$. The structure was solved by direct methods (SHELXTL) and refined by full-matrix least-squares refinement. Atomic coordinates, bond lengths and angles,a nd thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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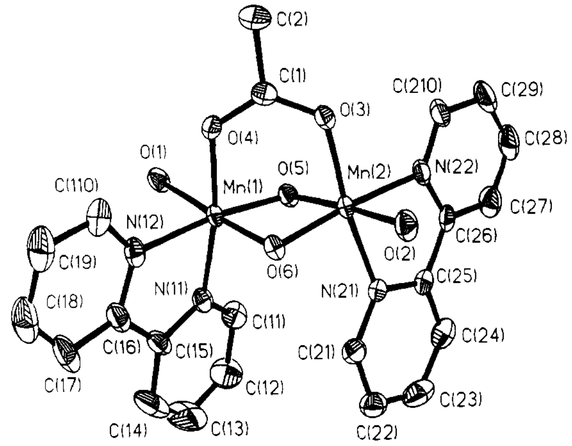

Figure 1. Structure and atom labeling scheme for **1**. Thermal ellipsoids are at the 30% probability level. Selected bond distances (Å) and angles (deg) are as follows: Mn(1)–O(4) = 1.925(4), Mn(11)–O(6) = 1.786(4), Mn(1)–N(12) = 2.054(5), Mn(1)–O(1) = 1.996(5), Mn(1)–O(5) = 1.802(4), Mn(1)–N(11) = 1.989(5), Mn(2)–O(2) = 1.986(5), MN(2)–O(5) = 1.793(4), MN(2)–N(21) = 2.000(5), Mn(2)–O(3) = 1.932(4), Mn(2)–O(6) = 1.796(4), Mn(2)–N(22) = 2.038(5); O(1)–Mn(1)–O(4) = 86.7(2), O(1)–Mn(1)–O(5) = 94.1(2), O(4)–Mn(1)–O(6) = 92.2(2), O(4)–Mn(1)–O(5) = 92.4(2), O(1)–Mn(1)–O(6) = 177.4(2), O(5)–Mn(1)–O(6) = 83.6(2), Mn(1)–O(6)–Mn(2) = 95.0(2), Mn(1)–O(5)–Mn(2) = 94.6(2), O(3)–Mn(2)–O(5) = 90.7(2), O(2)–Mn(2)–O(6) = 89.7(2), O(5)–Mn(2)–O(6) = 83.5(2), O(2)–Mn(2)–O(3) = 88.8(2), O(2)–Mn(2)–O(5) = 173.2(2), O(3)–Mn(2)–O(6) = 94.1(2).

$[Mn_2O_2(O_2CCH_3)(tpen)_2]^{3+}$ and $[Mn_2O_2(O_2CCH_3)(bpea)_2]^{3+}$.[22] In compound **1**, for the first time, a high-valent dimanganese core has retained both the terminal aquo ligands and an acetate bridge[23] upon oxidation to the (IV,IV) state.

The orientation of the two water molecules in **1** is *trans* such that a pseudo-C_2 axis passes through the center of the Mn_2O_2 plane. A *trans* geometry is also observed in the precursor **2**,[10] and in a trimer $[Mn_3O_4(H_2O)_2(bpy)_4]^{4+}$ (**3**) recently isolated by Thorp *et al.*[24] The latter, obtained by acidification of the mixed-valence dimer $[Mn_2O_2(bpy)_4]^{3+}$,[25] is the first known example of a Mn cluster possessing a Mn(IV)–aqua bond. The structure of **1** bears a close resemblance to that of **3**, which contains a bridging O–Mn^{IV}–O unit instead of the bridging acetate found in **1**. The Mn···Mn separation of 2.642 Å observed in **1** is typical of the Mn_2O_2 core and compares with the distance of 2.679 Å found in **3**, even though the O–C–O angle (123.9°) in bridging acetate of **1** is much larger as compared to the capping O–Mn–O angle (100.7°) in **3**.[24] This implies that the geometry of the $[Mn_2O_2]^{4+}$ core is predetermined by a combination of very strong covalent bonding between Mn(IV) and O^{2-} and a strong repulsion between highly charged Mn atoms in the Mn_2O_2 rhombus and remains essentially unperturbed by the steric requirements of additional bridging groups. The average Mn(IV)–OH_2 bond length of 1.991 Å compares well with that of 2.045 Å observed in **3**,[10] whereas it is significantly longer than the Mn(IV)–OH bond distance of 1.881 Å reported by Wieghardt *et al.*[9] The longer bond confirms that the bound species is an aquo group. The Mn(IV)–OH_2 bond distance in **1** is considerably shorter than Mn(III)–OH_2 bond length of 2.312 Å observed in the starting material **2** due to the higher positive charge of Mn(IV) in **1**.

The protons on the bound aquo group are strongly acidic, and **1** is found not be stable in aqueous medium. A millimolar solution obtained by dissolving **1** in water (pH 1.6), when titrated with standard NaOH, indicates that four protons per mole are liberated. The deprotonation step is irreversible, most likely leading to the formation of a stable higher nuclearity oxo aggregate.[26] If so, dimer **1** can be considered a potential precursor to multinuclear Mn clusters involving oxo bridges in aqueous media, where the proton ionization from the aquo moieties leads to a lowering of pH and, consequently, prevents the formation of the thermodynamically stable MnO_2. A complete structural and spectroscopic analysis of the deprotonated complex is currently in progress.

The absorption spectrum of **1** in CH_3CN shows only poorly-resolved shoulders (~425 and 615 nm) on the quickly rising toward ultraviolet background. The cyclic voltametry of **1** in CH_3CN with TBAP as the supporting electrolyte shows an irreversible wave at 0.33 V vs SCE corresponding to the (IV,IV)/(IV,III) reduction.[27] The temperature dependence of the magnetic moment (μ_{eff} per dimer) shows a decrease from 3.76 μ_B at 292 K to 0.49 μ_B at 16 K. These data imply significant antiferromagnetic coupling between the metal centers. Best fits gave $g = 2.000$, 0.33% of an impurity (assumed to be a mononuclear Mn^{2+}), and $J = -67$ cm^{-1}.

In conclusion, a new high-valent manganese complex has been structurally characterized, which contains bridging acetate and terminally ligated waters in one molecule. The stabilization of higher oxidation state Mn by bridging acetate should aid our understanding of the mechanism of water oxidation in OEC. Site-directed mutagenesis studies on PSII imply the potential involvement of carboxylate residues glutamate and aspartate as being essential for the efffective generation of dioxygen from water.[28] The highly electron donating environment on the Mn atoms in **1** and **2**, with three oxygen and two nitrogen donors leads to a stabilization of Mn–OH_2 bond through *two* sequential one-electron metal-centered oxidations. EPR, ESEEM, and ENDOR data show a predominance of oxygen-containing environment in the first coordination sphere of Mn atoms in PSII,[29] and a similar mechanism can be envisioned with the S state propagation taking place without oxidizing the bound water until the OEC reaches the metastable [S_4] state, as previously suggested.

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Supplementary Material Available: Tables of X-ray crystallographic data for compound **1** including a structure determination summary, atomic coordinates and thermal parameters, and bond distances and angles (9 pages). Ordering information is given on any current masthead page.

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