An Unusual Example of Multiple Proton-Coupled Electron Transfers in a High-Valent Oxomanganese Dimer, $[(\mathrm{phen})_2\mathrm{Mn}^{\mathrm{III}}(\mathrm{O})_2\mathrm{Mn}^{\mathrm{IV}}(\mathrm{phen})_2](\mathrm{ClO}_4)_3$ (phen = 1,10-Phenanthroline)

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Photosystem II (PS II) contains a tetramanganese oxo cluster which can undergo sequential redox steps leading to the oxidation of water to dioxygen.[1] Many proposed mechanisms for water oxidation involve protonation–deprotonation at the bridged oxo groups accompanied by oxidation or reduction of the metal centers. These proton-coupled electron transfer reactions provide pathways for the enzyme to regulate the kinetics and thermodynamics of water oxidation. Systematic investigations on net hydrogen atom transfer to the bridging oxo groups of inorganic manganese complexes in aqueous solutions thereby seem fruitful in attempting to reach a better understanding of the redox cycle of enzymes like PS II. In this work, we report an unusual example of multiple proton-coupled electron transfers in a single oxomanganese dimer, $[(\mathrm{phen})_2\mathrm{Mn}^{\mathrm{III}}(\mathrm{O})_2\mathrm{Mn}^{\mathrm{IV}}(\mathrm{phen})_2](\mathrm{ClO}_4)_3$ (**1**, phen = 1,10-phenanthroline).

Recently, we have studied[2–4] the electrochemical behavior of several high-valent oxomanganese dimers in aqueous media. For example, $[(\mathrm{bpy})_2\mathrm{Mn}^{\mathrm{III}}(\mathrm{O})_2\mathrm{Mn}^{\mathrm{IV}}(\mathrm{bpy})_2](\mathrm{ClO}_4)_3$ (**2**, bpy = 2,2′-bipyridine) shows a quasi-reversible oxidation wave at 1.26 V (SCE) in its cyclic voltammogram in acetonitrile that is assigned to the III,IV/IV,IV couple. In aqueous solution, **2** shows a pH-dependent couple, which can be assigned to eq 1. The pK_a of the

$$[(\mathrm{bpy})_2\mathrm{Mn}^{\mathrm{III}}(\mathrm{O})_2\mathrm{Mn}^{\mathrm{IV}}(\mathrm{bpy})_2]^{3+} + \mathrm{H}^+ + \mathrm{e}^- \rightarrow [(\mathrm{bpy})_2\mathrm{Mn}^{\mathrm{III}}(\mathrm{O})(\mathrm{OH})\mathrm{Mn}^{\mathrm{III}}(\mathrm{bpy})_2]^{3+} \quad (1)$$

III,III species was also estimated by comparison with the measurements made in acetonitrile solution,[2] and the aqueous electrochemistry of the complex was shown to depend on the nature of the electrode surface.[3] In contrast, measurements under similar conditions for $[(\mathrm{bispicen})\mathrm{Mn}^{\mathrm{III}}(\mathrm{O})_2\mathrm{Mn}^{\mathrm{IV}}(\mathrm{bispicen})](\mathrm{ClO}_4)_3$ (**3**, bispicen = *N,N′*-bis(2-methylpyridyl)ethane-1,2-diamine) show a kinetically decoupled proton–electron transfer, consistent with an EC mechanism.[4]

$$[(\mathrm{bispicen})\mathrm{Mn}^{\mathrm{III}}(\mathrm{O})_2\mathrm{Mn}^{\mathrm{IV}}(\mathrm{bispicen})]^{3+} + \mathrm{e}^- \rightarrow [(\mathrm{bispicen})\mathrm{Mn}^{\mathrm{III}}(\mathrm{O})_2\mathrm{Mn}^{\mathrm{III}}(\mathrm{bispicen})]^{2+} \quad (2)$$

$$[(\mathrm{bispicen})\mathrm{Mn}^{\mathrm{III}}(\mathrm{O})_2\mathrm{Mn}^{\mathrm{III}}(\mathrm{bispicen})]^{2+} + \mathrm{H}^+ \rightarrow [(\mathrm{bispicen})\mathrm{Mn}^{\mathrm{III}}(\mathrm{O})(\mathrm{OH})\mathrm{Mn}^{\mathrm{III}}(\mathrm{bispicen})]^{3+} \quad (3)$$

The difference in reactivity of the bpy and bispicen complexes may be a result of the differing pK_a of their respective oxo bridges arising from the donor properties of the ancillary ligands. There have been reports on multiple electron transfers in nonaqueous medium for oxomanganese clusters.[5,6]

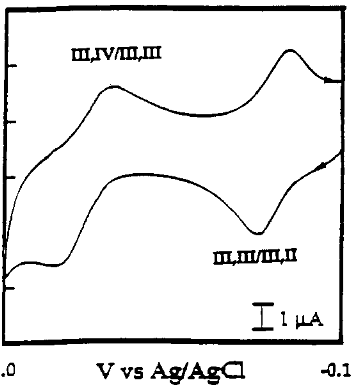

Figure 1. Cyclic voltammogram for $[(\mathrm{phen})_2\mathrm{Mn}^{\mathrm{III}}(\mathrm{O})_2\mathrm{Mn}^{\mathrm{IV}}(\mathrm{phen})_2](\mathrm{ClO}_4)_3$ in 0.1 M phosphate buffer at pH 4.5. Scan rate: 100 mV/s.

Cooper and Calvin[7] reported that the cyclic voltammogram of **1** shows two quasi-reversible waves at 0.335 and 1.26 V (SCE) in acetonitrile solution; the first corresponds to the reduction of the III,IV species to the III,III state and the second to the oxidation of the III,IV form to IV,IV. Two waves are retained when the complex is dissolved in 0.1 M phosphate buffer (Figure 1), but at different pH-dependent potentials.[8,9] The plot of the pH versus the $E_{1/2}$ potential for the higher-potential couple (III,IV/III,III) is linear with a slope of 0.079 ± 0.015 V/pH (Figure 2). This value is within experimental error of the ideal value of 0.059 V/pH appropriate for a $1\mathrm{H}^+/1\mathrm{e}^-$ process. The heterogeneous rate constant deduced using Nicholson's method[10] is $(2.5 \pm 1) \times 10^{-3}$ cm/s. This value is similar to that observed for the analogous reduction of **2** and in related pH-dependent couples based on aquaruthenium(II).[2,11] The lower-potential couple (III,III/III,II) shows similar behavior with changing pH. The slope of the Pourbaix diagram[12,13] (Figure 2), is 0.066 ± 0.015 V/pH. This value is also within experimental error of the value

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(9) **Experimental Section. Complex.** $[(\mathrm{phen})_2\mathrm{Mn}^{\mathrm{III}}(\mathrm{O})_2\mathrm{Mn}^{\mathrm{IV}}(\mathrm{phen})_2](\mathrm{ClO}_4)_3$ was prepared by a published procedure.[7] **Electrochemistry.** Cyclic voltammograms were recorded using a PAR 273 potentiostat. Glassy-carbon working electrodes were activated as described previously.[2] Activation was run for five cycles of 30 s at 1.8 V and 15 s at –0.2 V in 0.1 M sulfuric acid. A saturated calomel electrode was used as a reference with a Pt-wire auxillary electrode. The solutions were made in Milli-Q water with a complex concentration of 1–2 mM. The solutions were buffered with 0.1 M phosphate buffer, and the pH was adjusted by careful addition of 0.1 M NaOH or 0.1 M HNO_3 to the metal complex solution.

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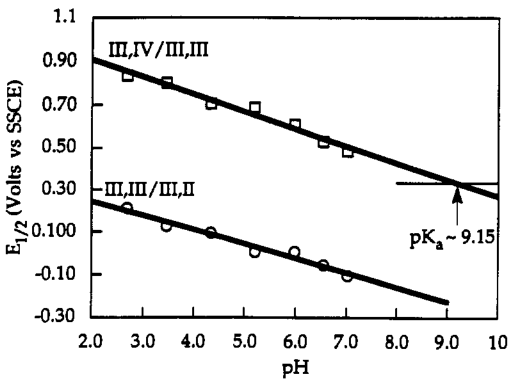

Figure 2. Pourbaix diagram for $[(phen)_2Mn^{III}(O)_2Mn^{IV}(phen)_2](ClO_4)_3$ in 0.1 M phosphate buffer. Solid horizontal line represents the potential of the III,IV/III,III couple in acetonitrile, which is assumed to represent the reduction of **1** without protonation.

for a one-proton/one-electron redox couple. The heterogeneous rate constant is $(7.5 \pm 1) \times 10^{-3}$ cm/s.

This is the first example of a bis(μ_2-oxo)manganese dimer which can reversibly protonate both of its oxo-bridges upon reduction. It is stable under the experimental pH conditions and, even after both oxo bridges are protonated, retains its solubility in aqueous solution. We therefore assign the two redox couples to eqs 4 and 5.

$$[(phen)_2Mn^{III}(O)_2Mn^{IV}(phen)_2]^{3+} + H^+ + e^- \rightarrow [(phen)_2Mn^{III}(O)(OH)Mn^{III}(phen)_2]^{3+} \quad (4)$$

$$[(phen)_2Mn^{III}(O)(OH)Mn^{III}(phen)_2]^{3+}\ H^+ + e^- \rightarrow [(phen)_2Mn^{III}(OH)_2Mn^{II}(phen)_2]^{3+} \quad (5)$$

The pK_a value of $[(phen)_2Mn^{III}(O)(OH)Mn^{III}(phen)_2]^{3+}$ can be estimated, from the slope of the Pourbaix plot and the value of the III,IV/III,III couple measured in acetonitrile, to be ~9.15 (Figure 2). This value is intermediate compared to the pK_a's of the hydroxo group in **2** ($pK_a = 11.0$)[3] and **3** ($pK_a = 8.35$).[4] It has been observed for **2** that the second protonation is not accessible due to the instability of the III,II bis(μ_2-hydroxo) species.[2] However for **3**, which has a much lower pK_a compared to that of **1** or **2**, the protonation is no longer kinetically coupled to electron transfer.[4] This would imply that the stability and consequent reversibility of protonation at the oxo-bridge of **1** is a direct result of the pK_a of the hydroxo bridge. Thus, the electronic effect of the ancillary ligand on the basicity of the oxo bridge determines the extent of protonation concerted with an oxidation change. An additional factor may be the flexibility the ligand. In our case, bpy may be more easily displaced compared to phen because of rotation of the two pyridyl rings.[14] This would render **2** vulnerable to any substitution by solvent or opening of the metal–ligand chelate.

Presented here is the observation of multiple proton-coupled electron transfers in a high-valent oxomanganese dimer. It is clear that the ancillary ligands affect directly the reversibility of the protonation of the oxo bridges concomitant with metal reduction. The comparison of the pK_a's of **1**, **2**, and **3** suggests that the steric bulk is a secondary effect compared to the basicity of the oxo groups. Oxidation of water by PS II is a four-electron/four-proton process. We have succeeded in extending our observation of a reversible one-electron/one-proton chemistry in **2** to two-electron/two-proton chemistry for **1**. Thus, for each metal center and each oxo bridge we can transfer one electron and one proton. Clearly, further extension to multiple redox processes will require more metal centers and more oxo bridges. Model studies of higher nuclearity clusters may give a deeper understanding of the process.

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