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[(H₂O)(terpy)Mn(μ-O)₂Mn(terpy)(OH₂)](NO₃)₃ (terpy = 2,2':6,2''-terpyridine) and its relevance to the oxygen-evolving complex of photosystem II examined through pH dependent cyclic voltametry

Clyde W. Cady[†], Katherine E. Shinopoulos, Robert H. Crabtree^{*}, and Gary W. Brudvig^{*}
Department of Chemistry, Yale University, PO Box 208107, New Haven, CT 06520-8107

Abstract

Photosynthetic water oxidation occurs naturally at a tetranuclear manganese center in the photosystem II protein complex. Synthetically mimicking this tetramanganese center, known as the oxygen-evolving complex (OEC), has been an ongoing challenge of bioinorganic chemistry. Most past efforts have centered on water-oxidation catalysis using chemical oxidants. However, solar energy applications have drawn attention to electrochemical methods. In this paper, we examine the electrochemical behavior of the biomimetic water-oxidation catalyst [(H₂O)(terpy)Mn(μ-O)₂Mn(terpy)(H₂O)](NO₃)₃ [terpy = 2,2':6',2''-terpyridine] (**1**) in water under a variety of pH and buffered conditions and in the presence of acetate that binds to **1** in place of one of the terminal water ligands. These experiments will show that **1** not only exhibits proton-coupled electron-transfer reactivity analogous to the OEC, but also may be capable of electrochemical oxidation of water to oxygen.

1.0 Introduction

In the past ten years, a number of manganese-based water oxidation catalysts have been identified.^{1–4} All of these new manganese catalysts are dimeric and all use two-electron oxygen-donor oxidants for catalytic turnover.^{5–7} The necessity of such oxidants as well as the need for multiple manganese atoms have been issues of interest due to the tendency of manganese complexes to disproportionate peroxides to give O₂ via a catalase pathway rather than by water oxidation,⁸ and due to the complexity inherent in multi-metal systems. To firmly establish the ability of manganese to oxidize water to oxygen, catalysis must be carried out using either a nonoxygen-donor oxidant or electrochemically, and a greater understanding of the necessary design elements must be reached.

The oxidation of water to oxygen using nonoxygen-donor oxidants such as Ce(IV) has been well established in the ruthenium literature.^{9–11} Due to the lack of any oxygen atom in the oxidant, O₂ must be formed from water. Unfortunately, in the history of manganese-based water oxidation, Ce(IV), and other similar oxidants, have generally failed to give catalytic O₂. The most recent attempts to use Ce(IV) as an oxidant have at best yielded no more than a single turnover of oxygen.^{6, 12, 13} It appears that oxidants such as Ce(IV) are often too acidic to be compatible with the basic oxo bridges of manganese dimers.¹²

^{*}Corresponding authors: gary.brudvig@yale.edu; robert.crabtree@yale.edu.

[†]Current address: Department of photochemistry and molecular science, Uppsala University, Box 523, 75237 Uppsala, Sweden

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To better understand why single-electron oxidants have been unsuccessful, we have studied the electrochemical behavior of the biomimetic water-oxidation catalyst $[(\text{H}_2\text{O})(\text{terpy})\text{Mn}(\mu\text{-O})_2\text{Mn}(\text{terpy})(\text{H}_2\text{O})](\text{NO}_3)_3$ [terpy = 2,2':6',2''-terpyridine] (**1**, Figure 1) in aqueous solution. Previous electrochemical studies of water-oxidizing manganese complexes have been hindered by both the scarcity of such complexes and the ubiquitous background oxidation of water to oxygen at the electrode. Past efforts to study **1** by electrochemical methods have characterized the main redox features of **1**.¹⁴ By studying the previously-characterized redox behavior of **1** as a function of pH and with different ligands bound in place of the terminal water(s), we aim to gain a better understanding of the factors that influence water oxidation using manganese. These electrochemical studies also provide insight into the differing roles of the two manganese ions in dimeric water-oxidation catalysis systems. A preliminary account of this work has been published.¹⁵

2.0 Experimental

2.1 Synthesis

$[(\text{H}_2\text{O})(\text{terpy})\text{Mn}(\mu\text{-O})_2\text{Mn}(\text{terpy})(\text{H}_2\text{O})](\text{NO}_3)_3$ (**1**, Figure 1) was prepared as published^{7, 16} in 52% yield. Elemental analysis $[(\text{terpy})\text{Mn}(\mu\text{-O})_2\text{Mn}(\text{terpy})(\text{H}_2\text{O})](\text{NO}_3)_3$, % calc (found): C, 44.35(44.53); N, 15.52(15.04); H, 2.98(2.94). $[(\text{bipy})_4\text{Mn}_2\text{O}_2](\text{ClO}_4)_3$ [bipy = 2,2'-bipyridine] (**2**, Figure 1) was prepared as published.¹⁷ Elemental analysis $[(\text{bipy})_4\text{Mn}_2\text{O}_2](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$, % calc(found): C, 42.53(43.28); N, 10.01(9.94); H, 3.42(3.10).

2.2 Electrochemistry

Electrochemical measurements were made on a EG&G Princeton Applied Research Model 273 potentiostat/galvanostat with a basal plane carbon working electrode, Pt counter electrode and a SCE reference electrode. The basal plane carbon working electrode was made by a procedure detailed in the supplementary material. Working electrodes were prepared for use by polishing with alumina powder and then resurfaced with tape to restore a textured grey basal surface.

All measurements were adjusted by +0.242 V to be reported as values vs. NHE. In this paper, all potentials are reported as the potential of the peak current for the oxidation of the complex in a cyclic voltammogram (CV) due to interference by Mn(II) with the reduction reaction in unbuffered solution, as detailed in the supplementary material.

All electrochemical solutions contained 0.1 M potassium nitrate as an electrolyte. Buffer solutions (4 mL) were made in 4 dram glass vials and the pH was adjusted using a dilute solution of nitric acid or potassium hydroxide in electrolyte. The buffer solution was then added to a second vial containing the compound being measured, sonication was used to aid in dissolving the compound if necessary, and the pH was checked and readjusted as needed. All electrochemical measurements were made within 10 minutes to reduce interfering background signals.

All chemicals, unless otherwise specified, were purchased from Aldrich and used as received. Elemental analysis was done by Atlantic Microlab Inc.

3.0 Results

3.1 Working electrode properties and assignment of peaks in CVs

While glassy carbon is the most common carbon electrode for electrochemistry, such as in the previous electrochemical characterization of **1** carried out by Baffert et al.,¹⁴ use of a basal plane graphite electrode allows for increased resolution of the electrochemical signals

owing to the decreased background water oxidation current under these conditions (Figure 2). Figure 3 shows the background CVs for the three different types of graphite electrodes: edge plane, glassy, and basal plane. Further information on the use of basal plane graphite electrodes can be found in the literature.¹⁸

The CV of **1** in aqueous solution is not reversible, with one anodic peak and two cathodic peaks that are assigned in Figure 2, as established by previous results.¹⁴ The positive anodic peak P_a^1 corresponds to the oxidation of the Mn(III,IV) dimer by one electron to Mn(IV,IV) followed by the increasing baseline corresponding to water oxidation at the electrode surface. The negative cathodic peaks P_c^1 and P_c^2 are assigned to the reduction of the Mn(IV,IV) dimer back to the Mn(III,IV) starting state (P_c^1), and to the reduction of a Mn(IV,IV,IV,IV) dimer-of-dimers species that is formed from dimerization of the Mn(IV,IV) species (P_c^2). The amplitude of P_c^2 increases at the expense of P_c^1 as the scan rate is decreased because the dimerization reaction occurs on the CV timescale, as shown previously.¹⁴

3.2 Proton coupled electron transfer and pK_a

To determine the role of protons in the oxidation of **1**, we compared the potential of the oxidation process of **1** and **2** with varied pH. The results shown in Figure 4 indicate that the (III,IV) to (IV,IV) oxidation potential of **1** (P_a^1) is variable with pH and that the potential of the oxidation process of **2** is independent of pH. The charge accumulated by the oxidation of **1** is balanced by the loss of a proton.^{19, 20} The fact that **1** shows a pH dependence while **2** does not allows assignment of the site of deprotonation. The pH dependence must be due to the only significant structural difference between the two complexes: the terminal water ligands on **1**. The protons on the terminal waters are responsible for the pH dependence of the oxidation, unlike earlier studies showing that protonation of an oxo bridge during reduction of the (III,IV) complex can result in a similar pH dependence.^{21, 22}

The difference in slope between complex **1** and **2** (Figure 4) also reveals significant information about the nature of the proton-coupled oxidation of **1**. The slope of the fit for **1** shows a 59 mV/pH slope, which indicates one proton is lost for every electron removed in the P_a^1 oxidation. The intersection of **1** and **2**, as shown in Figure 4, can also be interpreted as the pK_a for the Mn(IV,IV) oxidation state of **1** due to the similarity between the fully protonated **1** and **2**, both having similar coordination spheres and identical charge.

The pK_a of waters bound to manganese are of interest due to the difficulty of making similar measurements on the OEC. Table 1 shows the pK_a data from this paper along with literature values from other high-valent Mn complexes. The known pK_a 's for waters and μ -hydroxo groups bound to manganese are rather sparse, and the data for Mn(III) and Mn(IV) oxidation states reflect a wide variety of ligand systems. Our system represents a new addition to the small family of pK_a 's of terminal waters bound to high oxidation state multinuclear oxo-manganese complexes.

3.3 Ligand effects

In all of the experiments described above, the use of coordinating ligands was carefully avoided. The previous electrochemical characterization of **1** also avoided using any coordinating buffers.¹⁴ When studying a complex such as **1**, which has two easily displaceable terminal water ligands, avoiding coordinating buffers is sensible; however, almost all published procedures for oxygen evolution catalysis with **1** are done in the presence of acetate buffer.^{7, 16, 25} In this work, the electrochemical properties of **1** were examined in the presence of coordinating ligands. The results provide new mechanistic insights into the oxidation of water by **1** and suggest possible methods for its improvement.

The first experiment was to examine the pH dependence of P_a^1 in the presence of 50 mM acetate buffer. The addition of acetate buffer to the solution resulted in the lowering of the P_a^1 potential, as shown in Figure 5, while maintaining the 59 mV/pH slope observed in the unbuffered system. In conjunction with our earlier results showing that the 59 mV/pH slope must come from deprotonation of a terminal water ligand, this result leads to the conclusion that only one of the terminal waters on **1** is displaced by acetate in 50 mM acetate buffer. Further evidence for a single acetate interaction with **1** is provided by following P_a^1 as a function of acetate concentration (Figure 6). As Figure 6 shows, only one binding event, which is mostly complete after the addition of one equivalent, is observed out to 5 equivalents of acetate per **1**, and further extension of this graph out to 250 equivalents does not show evidence for a second binding event.

This single acetate binding in conjunction with earlier mechanistic studies in our lab²⁶ have led us to propose that **1** functions in a dissymmetric fashion. Acetate is proposed to bind to the Mn(IV), blocking the ligand-binding site at the higher oxidation state metal. This preferential binding of acetate to Mn(IV) aids in the reaction of **1** with oxone due to the proposed catalytic inactivity of Mn(IV) with two-electron oxidants such as oxone. The catalytic inactivity is proposed to arise because electron transfer between Mn(III) and Mn(IV) is slow in the mixed-valence complex and oxone cannot oxidize Mn(IV) to Mn(VI).²⁶ Therefore, catalytic activity requires that oxone binds to Mn(III) which is disfavored in the absence of acetate, but favored when acetate is bound to Mn(IV).

Acetate is not the only ligand to cause a decrease in the potential of P_a^1 while maintaining a 59 mV/pH dependence. Pyridine also has a very similar effect on the potential for oxidation of **1** (Figure 5). Observing that P_a^1 is lowered by acetate and pyridine when the pH is below their pK_a 's (Figure 5) indicates that the effect is likely due to binding and not hydrogen bonding. Hydrogen bonding would be different for the protonated and unprotonated forms of either acetate or pyridine, while acetate continues to have an equivalent effect at pH = 3.8, over half a pH unit below its pK_a . Below pH = 3.8, the values for P_a^1 are equivalent for **1** in unbuffered and in acetate or pyridine buffered solution (Figure 5), indicating that the pH is too low in these cases to allow coordination of acetate or pyridine to the complex.

Investigation of new coordinating ligands beyond acetate and pyridine was greatly hampered by the combination of pK_a and oxidative stability required for the experiment. For a successful screening, ligands must be deprotonated between pH 2–5 and must be able to withstand potentials in excess of 1 volt.

Finally, further examination of the CV of **1** in the presence of acetate buffer reveals an oxidation occurring at higher potential than P_a^1 . The CV of **1** in the presence of acetate shows a shoulder on the edge of the background current (Figure S6). Further work will be needed to characterize this oxidation in more detail, but in correlation with the decrease in the P_a^1 potential in the presence of acetate, this shoulder may be the oxidation of the Mn(IV,IV) complex to the formally Mn(IV,V) species that has been associated with formation of O_2 from water.

4.0 Discussion

We have described electrochemical experiments to determine the pH dependence of the oxidation of **1**. These measurements have allowed us to elucidate not only the proton-coupled oxidation of the mixed-valent Mn(III,IV) species to Mn(IV,IV) but also have helped to clarify the mechanism of water oxidation by **1** in acetate buffer.

Measurement of the pH-dependent oxidation of **1** shown in Figure 4 demonstrates the proton-coupled oxidation of **1**. Comparison of the pH dependence of **1** to the behavior of **2**

illustrates that the observed pH dependence must be attributed to the terminal water ligands found in **1** but not in **2**. Once the source of the pH change was determined, the slope of the pH vs. potential illustrated that only one proton was removed for every electron, even in the high charge environment experienced by **1**. These two observations alone allow us to establish **1** as an excellent mimic for the OEC of photosystem II in that it has a terminal water bound to the active site that exhibits the capability of losing a proton in concert with the loss of an electron so that the overall charge of the complex is maintained. The other coordination site can be occupied by acetate or pyridine, causing a lowering in the potential of the oxidation process. These two coordination sites of **1** are very analogous to the coordination properties the OEC in PSII. Similar electrochemical behavior has also been observed with chloride.²⁷

By examining the intersection of the pH vs. potential slope for **1** and **2**, we are able to estimate the pK_a value for the terminal water on **1** to be ~ 1.8 . For the pyridine- or acetate-bound complex **1**, the analogous intersection is shifted to $pH \sim 0.0$, which we assign as the pK_a of the $[Mn_2(\mu-O)_2(terpy)_2(H_2O)(py)]^{4+}$ complex (Table 1). The pool of known pK_a values for terminal waters attached to high-valent manganese complexes is quite small, as can be seen in Table 1. Finding a correlation between the known data at this time is very challenging. It appears that factors such as ligand charge and the coordination sphere have a great influence upon the pK_a of a terminal water on manganese. Accurate measurement of the pK_a of terminal waters in high-valent manganese model complexes is very important for accurate calculations to be carried out on the water-oxidation mechanism of the OEC.²⁸

Further examination of the pH range of Figure 4 allows us to propose a reason for the lack of success with oxidants such as Ce(IV). Figure 4 shows that the pH dependence of **1** only extends down to pH 2, while the typical operating pH of Ce(IV) solutions is no higher than pH 2; therefore, oxidation of the Mn(III,IV) species by an acidic solution of Ce(IV) will not be associated with deprotonation of the terminal water ligand, resulting in a higher potential for the subsequent oxidation of the complex to the formal Mn(IV,V) species necessary to activate the bound water for O-O bond formation.

With the established importance of the pH effect, it is logical that the next step in an examination of pH-dependent oxidation is buffer variability. Unfortunately, only a small number of buffers were able to be tested due to the extremely challenging conditions posed by an aqueous system with greater than 1 volt applied potential.

As shown in Figure 5, both pyridine and acetate cause a marked shift in the potential for oxidation of **1**. The ability of these two buffers to bind even slightly above their respective pK_a values indicates that both buffers are binding as ligands directly to **1**. The pH-dependent slope, shown in Figure 4, is maintained even after binding, indicating that only one terminal water on **1** is displaced by a buffer molecule. To further establish that only one of the two terminal waters on **1** is displaced by exogenous ligands, a titration curve was measured, as shown in Figure 6. An interesting feature of this binding is the large drop in the potential for oxidation of **1** upon binding either pyridine or acetate. It is expected that the exogenous, electron-donating ligand will bind to the Mn(IV) binding site, while the Mn(III) will be the site of oxidation and proton loss. This rather large shift caused by a ligation change at a remote metal raises questions as to the effect of minor coordination changes at any one of the four manganese atoms found in the OEC.

Finally, we address the issue of electrochemical water oxidation. Previous investigation of the oxidation of **1** has only shown a single oxidation step, but, with the addition of acetate, we have shown that the potential for oxidation of **1** can be decreased. Further examination of

1 in the presence of acetate shows the presence of a possible second oxidation wave, as shown in Figure S6. Further work is needed to fully characterize this second oxidation wave.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.
Structures of complexes **1** (left) and **2** (right).

Figure 2.

The CV of **1** at basal plane graphite (1 cm²) in H₂O + 0.1 M KNO₃ scanned at 40 mV/s. The redox reactions corresponding to each CV peak are schematically represented on the right.

Figure 3. Cyclic voltammograms of 0.1 M KNO_3 in water scanned at 40 mV/s showing the background oxidation of water to O_2 at three different carbon electrode surfaces: edge plane (red), glassy (blue), and basal plane (black). For each, two sequential CVs are shown.

Figure 4.

A pH vs. potential plot of the P_a^1 peak of **1** in unbuffered aqueous solution (open circles) and in an aqueous solution buffered with 50 mM terpy (open squares). The cyclic voltammetry peak corresponding to the oxidation of **2** in an aqueous solution buffered with 50 mM bipy is represented by crosses. The lines are linear least-squares fits to the data.

Figure 5.

Plot of the potential of Pa^1 vs. pH showing **1** in unbuffered aqueous solution (circles), **1** in an aqueous solution buffered with 50 mM acetate (open squares) and **1** in an aqueous solution buffered with 50 mM pyridine (filled squares). All CVs taken at a basal plane graphite electrode in $\text{H}_2\text{O} + 0.1 \text{ M KNO}_3$ and 1.0 mM **1** scanned at 40 mV/s. The lines are linear least-squares fits to the data.

Figure 6.

Effect of titration of acetate into a 2 mM solution of **1** on the potential of P_a^1 . All CVs taken at a basal plane graphite electrode in $H_2O + 0.1\text{ M KNO}_3$ pH = 4.3 scanned at 40 mV/s.

Table 1

pK_a's of terminal waters and μ-hydroxos bound to manganese.

HO coordination	Complex ^a	Mn Oxidation state	pK _a	Reference
Terminal water	[Mn ₃ (μ-O) ₄ (phen) ₄ (H ₂ O) ₂] ⁴⁺	Mn(IV,IV,IV)	4.0	23
Terminal water	[Mn ₂ (L) ₂ (H ₂ O)]	Mn(III,III)	19–20	20
Terminal water	[Mn ₂ (L) ₂ (H ₂ O)] ⁺	Mn(III,IV)	10–11	20
Terminal water	[Mn ₂ (L) ₂ (H ₂ O)] ²⁺	Mn(IV,IV)	<0	20
Terminal water	[Mn ₂ (μ-O) ₂ (terpy) ₂ (H ₂ O) ₂] ⁴⁺	Mn(IV,IV)	~1.8	This work
Terminal water	[Mn ₂ (μ-O) ₂ (terpy) ₂ (H ₂ O)(py)] ⁴⁺	Mn(IV,IV)	~0.0	This work
Terminal water	[Mn(porph)(H ₂ O) ₂]	Mn(IV)	1.8	24
Terminal water	[Mn(porph)(H ₂ O) ₂] [−]	Mn(III)	4.4	24
μ-OH	[Mn ₂ (μ-O)(μ-OH)(bipy) ₄] ³⁺	Mn(III,IV)	2.3	21
μ-OH	[Mn ₂ (μ-O)(μ-OH)(bipy) ₄] ²⁺	Mn(III,III)	11.0	21
μ-OH	[Mn ₂ (salpn) ₂ (μ-O)(μ-OH)] ⁺	Mn(IV,IV)	13.4	19
μ-OH	[Mn ₂ (salpn) ₂ (μ-O)(μ-OH)]	Mn(III,IV)	24.5	19
μ-OH	[Mn ₂ (salpn) ₂ (μ-OH)(μ-OH)] ²⁺	Mn(IV,IV)	6.5	19

^a phen = 1,10-phenanthroline; L = 2-hydroxy-1,3-bis(3,5-X₂-salicylideneamino)propane; py = pyridine; porph = 5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphyrin; salpn = N,N'-bis(salicylidene)-1,3-propanediamine