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The effect of protonation on $[Mn(IV)(\mu_2\text{-}O)]_2$ complexes

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Abstract

The series of complexes $[Mn(IV)(X\text{-}SALPN)(\mu_2\text{-}O)]_2$, **1**: X = 5-$OCH_3$; **2**: X = H; **3**: X = 5-Cl; **4**: X = 3,5-diCl; **5**: X=5-NO_2, contain $[Mn_2O_2]^{4+}$ cores with Mn–Mn separations of 2.7 Å. These molecules can be protonated to form $[Mn(IV)(X\text{-}SALPN)(\mu_2\text{-}O,OH)]_2^+$ in which a bridging oxide is protonated. The pK_a values for the series of $[Mn(IV)(X\text{-}SALPN)(\mu_2\text{-}O,OH)]_2^+$ track linearly versus the shift in redox potential with a slope of 84 mV/pKa. This observation suggests that the $[Mn_2O_2]^{4+}$ core can be considered as a unit in which the free energy of protonation is directly related to the ability to reduce the Mn(IV) ion. The marked sensitivity of the reduction potential to the presence of protons presents a mechanism in which an enzyme can control the oxidizing capacity of an oxo manganese cluster by the degree and timing of oxo bridge protonation.

Abbreviations: $AnH^+CF_3SO_3^-$ – anilinium triflate; DMA – N,N-dimethyl acetamide; H_2SALPN – 1,3-bis(salicylideneiminato)propane; H_2(5-Cl-SALPN) – 1,3-bis(5-chlorosalicylideneiminato)propane; H_2(3,5-diCl-SALPN) – 1,3-bis(3,5-dichlorosalicylideneiminato)propane; H_2(5-NO_2-SALPN) – 1,3-bis(5-nitorosalicylideneiminato)propane; H_2(5-OMe-SALPN) – 1,3-bis(5-methoxysalicylideneiminato)propane; $LuH^+CF_3SO_3^-$ – 2,4-lutidinium triflate; $Me_3NH^+Ph_4B^-$ – trimethylammonium tetraphenylborate; OEC – oxygen evolving complex; $PyH^+ClO_4^-$ – pyridinium perchlorate; SCE – saturated calomel electrode

Over twenty years ago, Pierre Joliot discovered the period four oscillation of oxygen evolution and Bessel Kok developed the model for what has become the accepted kinetic mechanism for oxygen evolution by photosystem II (Joliot and Kok 1975). This model invokes five oxidation levels for the enzyme, called S states, that are specified as S_0– S_4 depending on the number of stored oxidizing equivalents (S_4 being the most highly oxidized). Oxygen is released only on the $S_3 \rightarrow S_4 \rightarrow S_0$ transition. Most workers agree that four manganese ions are required for oxygen evolution (Debus 1992). Although the site of enzyme oxidation for each S state has been a topic of much debate, it is likely that, at least from S_0 to S_3, the manganese center is the redox active component (Ono et al. 1992). The redox active manganese ions are probably arranged in a single metal ensemble with suggested structural motifs ranging among 'dimer of dimers,' 'butterfly' or 'cubane.' Two points regarding the manganese ions that are of apparent agreement include the manganese oxidation states in each of the lower S states and the conservation of a di-μ_2-O^{2-} core bridging some of the Mn ions. The presently favored oxidation levels as a function of the lower S states are:

$S_0 = Mn(III)_3Mn(IV)_1$;

$S_1 = Mn(III)_2Mn(IV)_2$;

$S_2 = Mn(III)_1Mn(IV)_3$;

$S_3 = Mn(IV)_4$.

These assignments are consistent with a mixed valent

cluster in S_2 giving rise to a g = 2 multiline feature in the low temperature EPR spectrum (Dismukes and Siderer 1981). A one flash delayed 'cycle of four' pattern for observation of the multiline signal directly implicates manganese in the catalytic cycle. The EXAFS spectra of S_1 and S_2 clearly indicate a Mn–Mn vector at 2.7 Å, a separation that is diagnostic of $[Mn(IV)(\mu_2\text{-}O)]_2$, $[Mn(IV)Mn(III)(\mu_2\text{-}O)_2]$ and very closely related structures (Larson et al. 1992)

While the oxidation states of the enzyme are clearly linked to sequential photodriven oxidations of a manganese cluster, the proton release pattern is not as simple. Wille and Lavergne have shown (1982) that proton release within thylakoids is oscillatory. Certain complications, such as the possibility of proton release under conditions when no oxygen is evolved, make determination of proton release stoichiometry difficult. An experiment using the amphiphilic dye Neutral red indicated that the stoichiometry of proton release is 1:0:1:2 corresponding to the $S_0 \rightarrow S_1$, $S_1 \rightarrow S_2$, $S_2 \rightarrow S_3$, $S_3 \rightarrow S_4$, S_0 cycle in rigorously dark adapted sites. (Förster et al. 1981, Wille and Lavergne 1982). However, a reinterpretation of the proton release experiments with Neutral red has implicated a strongly pH dependent non-integer stoichiometry (Jahns et al. 1991); while in another experiment a pattern of 1:1:1:1 was found (Jahns et al. 1992).

While the proton release stoichiometry is still a matter of disagreement, and the manganese oxidation cycle is thought to be 1:1:1:1, it is possible that each electron transfer event is not coupled to a protonation/deprotonation event at the catalytic cluster. Toward that end understanding the impact of protonation of a $[Mn(IV)(\mu_2\text{-}O)]_2$ core on the redox potential, structure and magnetic exchange would be extremely useful. Thorp et al. (1989) have shown that electron transfer at a Mn oxo dimer can be coupled to a proton transfer event and Carroll and Norton (1992) have demonstrated that proton transfer to an oxygen in a Mn–O–Mn unit is relatively slow. Clearly, protonation of a $[Mn(IV)(\mu_2\text{-}O)]_2$ structure can have significant kinetic and thermodynamic consequences on the enzymatic process.

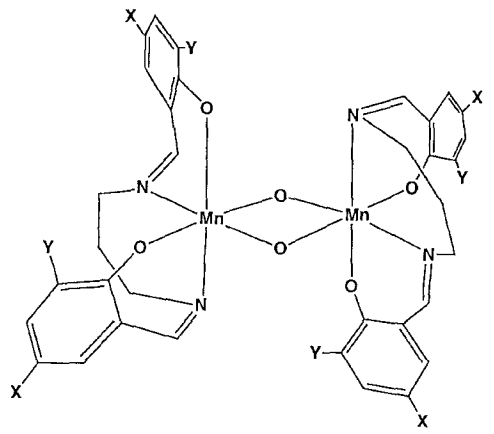
We have previously described the rich chemistry of the $Mn(IV)(\mu_2\text{-}O)$ dimer $[Mn(IV)SALPN(\mu_2\text{-}O)]_2$ (Larson and Pecoraro 1991a,b). This material has an $[Mn(IV)(\mu_2\text{-}O)]_2^{4+}$ core with Mn ions separated by 2.73Å. This molecule reacts with $H_2{}^{18}O_2$ in a catalase reaction liberating $^{18}O_2$. We have suggested that this complex could directly model the reactivity of the S_0 to S_2 catalase reaction that can be observed with the oxygen evolving complex (Frasch and Mei 1987, Frasch 1992) and also could explain half of the reaction for dioxygen production in a 'dimer of dimers' structural model. Addition of a proton to this complex forms $[Mn(IV)SALPN(\mu_2\text{-}O,OH)]_2^+$ leading to an increase in Mn–Mn separation to 2.81Å, a decrease in the magnetic exchange interaction and dramatic inhibition of the catalase activity (Larson et al. 1992). We felt that this would be an excellent system to explore the chemistry of protonated $[Mn(IV)(\mu_2\text{-}O,OH)]$ dimers. In this report we will address the basicity of the bridging oxo group as a function of ligand donating capacity to manganese and describe an interesting correlation between acid dissociation and complex redox potential. This information should be extremely helpful in establishing how protonation may affect catalysis of water oxidation.

Materials and methods

Materials. Salicylaldehyde, 5-chlorosalicylaldehyde, 3,5-dichlorosalicylaldehyde, 5-nitrosalicyladehyde, 5-methoxysalicylaldehyde and 1,3-diaminopropane were obtained from Aldrich Chemical Co. Hydrogen peroxide was from Malinckrodt. All other chemicals and solvents were reagent grade.

Preparation of compounds. The series of ligands was prepared by the Schiff base condensation of the appropriately substituted salicylaldehyde with 1,3-diaminopropane. The series of complexes $[Mn(IV)(X\text{-}SALPN)(\mu_2\text{-}O)]_2$, **1**: X = 5-$OCH_3$; **2**: X = H; **3**: X = 5-Cl; **4**: X = 3,5-diCl; **5**: X = 5-NO_2, shown in Fig. 1, was prepared by the reaction of Mn(III)(X-SALPN) precursors with hydrogen peroxide to form the complexes, $[Mn(IV)(X\text{-}SALPN)(\mu_2\text{-}O)]_2$, as previously described (Larson and Pecoraro 1991b). The protonated materials were prepared in situ by addition of a stoichiometric amount of acid of sufficient acidity to cleanly protonate the complex.

The acids that were used for the titrations were



	1	2	3	4	5
X =	OMe	H	Cl	Cl	NO_2
Y =	H	H	H	Cl	H

Fig. 1. Schematic drawing of the structures of the [Mn(IV)(X-SALPN)(μ_2-O)]$_2$ complexes **1** to **5**.

prepared by reaction of the appropriate N-donor base with triflic acid or perchloric acid in ethanol or acetone and recrystallized from ethanol and ether. The exception to this procedure was for trimethylammonium tetraphenylborate which was used as received from Aldrich. (*Caution:* Perchlorate salts may be explosively unstable! Do not take such salts to dryness.) Concentrated sulfuric acid (11.2 M) was diluted to 4 mM in acetonitrile for use. Aliquots of acetonitrile solutions of the acids were added to the acetonitile solutions of the Mn complexes for the titrations. The pK_as for these acids in acetonitrile have been reported as follows: $AnH^+CF_3SO_3^-$, pK_a = 10.6 (Coetzee and Padmanabhan 1965); $PyH^+ClO_4^-$, pK_a = 12.3 (Coetzee and Padmanabhan 1965); $LuH^+CF_3SO_3^-$, pK_a=14.05 (Izutsu 1990); $Me_3NH^+Ph_4B^-$, pK_a = 17.6 (Coetzee and Padmanabhan 1965); sulfuric acid, pK_a = 7.25 (Kolthoff et al. 1961).

Methods. UV-vis spectra were recorded on a Perkin-Elmer Lambda 9 UV/vis/NIR spectrophotometer equipped with a Perkin-Elmer 3600 data station. Spectrophotometric titrations were performed by adding an appropriate acid with a non-coordinating anion to an acetonitrile solution of [Mn(IV)(X-SALPN)(μ_2-O)]$_2$. The pK_a values were determined using the change in absorbance at the λ_{max} for the protonated complex (e.g., 530 nm, ε = 7700 M^{-1} cm^{-1} for $\mathbf{1H^+}$). The pK_a values were calculated using Eq. (1):

$$K_a(\text{complex}) = K_a(\text{acid}) / K_{eq} \quad (1)$$

where K_a(complex) = $[H^+][Mn_2O_2]/[Mn_2(O,OH)^+]$, K_a(acid) is from the reported pK_a of the acid HB^+ in acetonitrile (vide supra), and K_{eq} = $[B][Mn_2(O,OH)^+]/[HB^+][Mn_2O_2]$ is determined spectrophotometrically.

Similar titrations were completed in CH_2Cl_2. Quantitative determination of complex acidity could not be obtained in CH_2Cl_2 since the precise acidities of appropriate acids have not been tabulated for this solvent; however, the same trends in protonation were observed (e.g., $AnH^+CF_3SO_3^-$ can protonate **3** while $LuH^+CF_3SO_3^-$ can not).

Electrochemical measurements were carried out using a BAS-100 electrochemical analyzer. Dimethylacetamide (DMA) was used as received from Aldrich. Acetonitrile and methylene chloride were received from Burdick and Jackson and were not further purified. The supporting electrolyte used was tetrabutylammonium hexafluorophosphate ($TBAPF_6$) and was prepared from tetrabutylammonium bromide and ammonium hexafluorophosphate in acetonitrile, then recrystallized from ethanol. All measurements are reported versus the saturated calomel electrode (SCE) and standardized with the ferricinium/ferrocene couple.

Results

Upon protonation by an acid with a non-coordinating anion, a shoulder in the absorption spectrum (e.g., for **1**, 480 nm, ε = 7100 M^{-1} cm^{-1}) disappears and a lower energy absorption band grows in (e.g., for $\mathbf{1H^+}$, 530 nm, ε = 7700 M^{-1} cm^{-1}). The titrations were performed in organic solvents as the protonated complexes decompose in water. Acetonitrile was selected as the standard solvent since there are a significant number of weak acids for which the pK_a has been reported. Although the solubilities of **1** to **5** in acetonitrile are limited, they are sufficient for the spectrophotometric titrations due to the large molar extinction coefficients of the absorption bands. Table 1 provides a list of the pK_as determined spectrophotometrically for the series [Mn(IV)(X-

Table 1. Reduction potentials and acid dissociation constants for $[Mn(IV)(\mu_2\text{-}O)L]_2$ and $[Mn(IV)(\mu_2\text{-}O,OH)L]_2^+$

$[Mn(IV)(\mu_2\text{-}O)L]_2$	**1**	**2**	**3**	**4**	**5**
Reduction potential[a]	–588	–507	–335	–235	+20
$[Mn(IV)(\mu_2\text{-}O,OH)L]_2^+$	**1**	**2**	**3**	**4**	**5**
pK_a[b]	14.1(0.4)	13.4(0.2)[c]	11.5(0.4)	10.8(0.3)	6.8(0.3)
Acid[d]	LuH^+,Me_3NH^+	LuH^+,PyH^+	AnH^+,PyH^+	AnH^+	H_2SO_4
λ_{max} (nm)	580	535	555	520, 590	525

[a] Determined in CH_2Cl_2, $E_{1/2}$ reported in millivolts vs. the standard calomel electrode (SCE). Since the reduction of **5** is irreversible, the value is estimated from the potential of the reductive wave and the ΔE's of **1** to **4**.
[b] Determined in acetonitrile. Range given in parenthesis.
[c] This value has been previously measured as 13.0 (J.M. Carroll and J. R. Norton, personal communication).
[d] Acid used for spectrophotometric titration. Their pK_as in acetonitrile are given in the text.

SALPN)(μ_2-O)]$_2$ in acetonitrile using Eq. (1). Complexes **1** to **5** are protonated in a well behaved manner as illustrated by the titration of **2** with LuH^+ in Fig. 2. The isosbestic point at 490 nm demonstrates that [Mn(IV)(SALPN)(μ_2-O)]$_2$ and [Mn(IV)(SAL-PNμ_2-O,OH)]$_2^+$ are the only species in solution.

The reduction potentials of the Mn(IV/IV)/Mn(III/IV) couples for complexes **1** to **5** are reported in Table 1. The reductions of **1** to **4** in methylene chloride are quasireversible with ΔE's around 120 mV (ΔE for the ferricinium/ ferrocene couple is measured as 100 mV under these conditions). The reduction of **5** is not reversible, so the value reported for $E_{1/2}$ in Table 1 is estimated from the position of the reductive wave and the ΔE's of **1** to **4**. In DMA, none of the reductions appear to be reversible, however the shift in potential of the reductive wave between complexes **1** to **5** is similar to that in methylene chloride. No reversible electrochemistry is observed that is assignable to the Mn(IV/IV)/Mn(III/IV) couple for the protonated complexes $\mathbf{1H^+}$ to $\mathbf{5H^+}$. Experiments involving the addition of stoichiometric and substoichiometric amounts of acids of varying pK_a to solutions of the Mn(III/IV) dimers $\mathbf{1^-}$ to $\mathbf{5^-}$ are currently in progress in order to understand the irreversibility of this electrochemical process.

Discussion

The [Mn(IV)(X-SALPN)(μ_2-O)]$_2$ complexes **1** to **5** provides a series of structurally analogous $[Mn_2O_2]^{4+}$ cores with the identical first coordination sphere for the manganese ions. The phenyl ring substituents

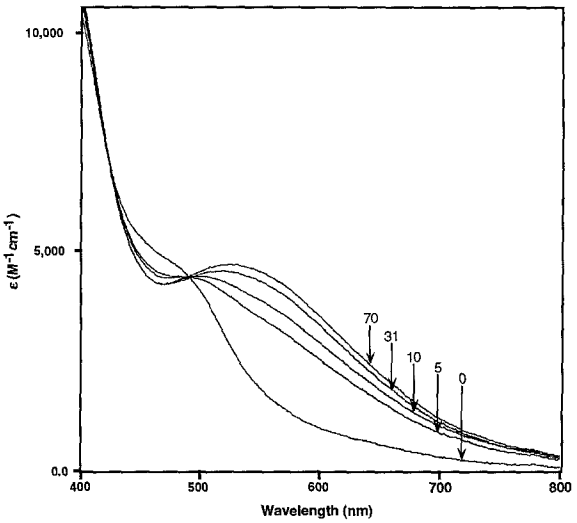


Fig. 2. Absorption spectra following the titration of **2** with $LuH^+CF_3SO_3$, with the number of equivalents of added LuH^+. The isosbestic point is at 490 nm.

markedly perturb the electronic structure of the manganese as is illustrated by the large range of reduction potentials (over 600 mV) for **1** to **5** and acid dissociation constants (range of > 7 pK_a units) for the protonated derivatives $\mathbf{1H^+}$ to $\mathbf{5H^+}$. Figure 3 shows the pK_as of $\mathbf{1H^+}$ to $\mathbf{5H^+}$ (e.g., as given for [Mn(IV)(SALPN)(μ_2-O, OH)]$_2^+$ in Eq. (2)) plotted versus the reduction potentials of **1** to **5** (e.g., as given for [Mn(IV)(SALPN)(μ_2-O)]$_2$ in Eq. (3)).

$$\mathbf{2H^+} \rightarrow \mathbf{2} + H^+ \quad (2)$$

$$\mathbf{2} + e^- \rightarrow \mathbf{2^-} \quad (3)$$

Included in this diagram are the potentials for **1** to **3**

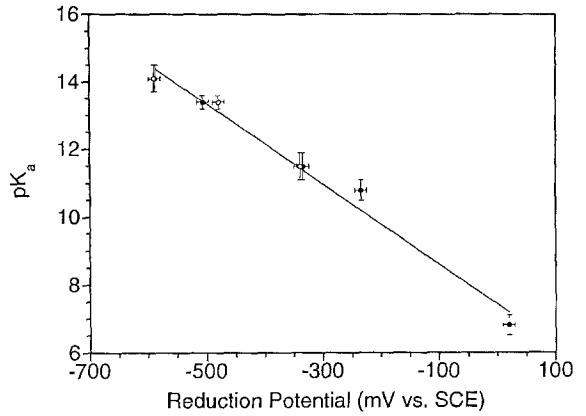


Fig. 3. Plot of pK_a of $\mathbf{1H^+}$ to $\mathbf{5H^+}$ vs. reduction potential of **1** to **5**. Potentials are measured vs. SCE (241 mV compared to SHE). Solid circles represent data from this work, and open circles represent the potentials reported previously (Horwitz et al. 1993) plotted against the pK_as measured in this work. The line represents the linear least squares fit of the solid circles, with a slope corresponding to 84 mV/pK_a unit.

reported by Horwitz (Horwitz et al. 1993). This relationship is clearly linear over the entire range of complexes, with a slope corresponding to 84 mV/pK_a unit.

This linear relationship is an indication of the strong electronic coupling of the $[Mn_2O_2]^{4+}$ core. The equation for the electrochemical process is:

$$E_f = E_{[Mn_2O_2]4+} - 0.059 \log (K_L) \quad (4)$$

in which E_f is the formal potential in volts for the $[Mn(IV)(X\text{-}SALPN)(\mu_2\text{-}O)]_2$ reduction given as Eq. (3), $E_{[Mn_2O_2]4+}$ is the standard potential for an $[Mn_2O_2]^{4+}$ core, and K_L is the binding constant of X-SALPN to $[Mn_2O_2]^{4+}$. The affinity of a series of structurally analogous ligands such as X-SALPN for $[Mn_2O_2]^{4+}$ is going to be dominated by the basicity of the donor ligands, with the stronger donors (e.g., **1**) showing greater affinity than the weaker donors (e.g., **5**). In the limiting case where $[Mn_2O_2]^{4+}$ is a strongly coupled unit, the electron density changes associated with each ligand will affect all atoms of the core as one unit. The reduction potential is a probe of the manganese electronic environment and the K_a (the acid dissociation constant for the process in Eq. (2)) reflects electron density at the μ_2-O bridges. In this case, Eq. (4) is more closely related to Eq. (5), and one should observe a linear relationship with

$$E_f = E_{[Mn_2O_2]4+} - 0.059 \log (K_a) \quad (5)$$

a slope of 59 mV/pK_a unit. Stated another way, the electron donation of the ligand to such a strongly coupled $[Mn_2O_2]^{4+}$ core impacts the entire unit rather than atoms individually. Thus, the free energy change for protonation of the $[Mn_2O_2]^{4+}$ system, reflecting electron density on the bridging oxo groups, is related in a linear one-to-one correspondence to the free energy change for reduction of this core, reflecting electron density on the manganese ions. Such a relationship should not be confused with a coupled one-electron/one-proton transfer. A slope of 59 mV is predicted by the Nernst equation for a coupled one electron/one proton transfer, as observed in Pourbaix diagrams where the dependence of reduction potential on pH of the solution is plotted. However, that is not the experiment reported here as *the reduction and protonation of the complexes are observed independently*. The irreversibility of the reduction of $\mathbf{1H^+}$ to $\mathbf{5H^+}$ indicates that the relationship between proton transfer and electron transfer in these complexes is more complicated than the simple relationship observed in standard Pourbaix diagrams.

The pK_as reported in Table 1 were determined in acetonitrile, however the aqueous pK_a values may be estimated to be –0.7 to +6.6 for $\mathbf{5H^+}$ to $\mathbf{1H^+}$, as Norton has suggested that for large molecules the aqueous pK_a is about 7.5 ± 1 pK_a units lower than in acetonitrile (Kristjánsdóttir and Norton 1992). Thus, these complexes provide examples of Mn_2O_2 units with a range of physiologically relevant pK_as that would require a strong acid for protonation in aqueous solution to those that may be easily protonated by an acid as weak as histidine or aspartic/glutamic acids. Since the pK_a associated with a second protonation would be significantly lower (about 5 pK_a units is typical for most oxyacids), this would only allow for a second protonation of a $[Mn(IV/IV)_2(O,OH)]$ unit if the reduction potential was near the most negative extreme of the complexes in this series.

In a previous report, (Larson et al. 1992) we suggested that the potential of the protonated $[Mn(IV)(X\text{-}SALPN)(\mu_2\text{-}O)]_2$ ($\mathbf{2H^+} + 1\ e^- \rightarrow \mathbf{2H}$) was nearly 500 mV more positive than the potential for the unprotonated species ($\mathbf{2} + e^- \rightarrow \mathbf{2^-}$). Such a startling shift in potential upon protonation underscores the notion that protons and protonation states

of oxo manganese clusters will dramatically influence the oxidizing power of the catalytic center. For example, much of the oxidizing power of a system would be lost if a proton was released from a MnO cluster simultaneous to oxidation of the cluster. This provides a mechanism for generating a high valent, but non-oxidizing center for lower S states where premature oxidation reactions are nonproductive. In this way, several oxidation equivalents may be accumulated without unwanted redox reactions. In contrast, simultaneous protonation and oxidation of an MnO cluster can convert an electrochemically stable site into an extremely oxidizing center in a single step. Thus, protonation, or strong hydrogen bond formation, with an MnO center in the later S states, when all necessary oxidizing equivalents are available, could trigger an oxidation event. Further studies using the [Mn(IV)(X-SALPN)(μ_2-O)]$_2$ complexes should clarify the magnitude of this redox perturbation.

Acknowledgements

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References

Carroll JM and Norton JR (1992) Protonation of a bridging oxo ligand is slow. J Am Chem Soc 114: 8744–8745

Coetzee JF and Padmanabhan GR (1965) Properties of bases in acetonitrile as solvent. IV. Proton acceptor power and homoconjugation of mono- and diamines J Am Chem Soc 87: 5005–5010

Debus RJ (1992) The manganese and calcium ions of photosynthetic oxygen evolution. Biochim Biophys Acta 1102: 269–352

Dismukes GC and Siderer Y (1981) Intermediates of a polynuclear manganese center involved in photosynthetic oxidation of water. Proc Natl Acad Sci USA 78: 274–278

Förster V, Hong Y-Q and Junge W (1981) Electron transfer and proton pumping under excitation of dark-adapted chloroplasts with flashes of light. Biochim Biophys Acta 638: 141–152

Frasch WD (1992) Alternate substrates as probes for the mechanism of the oxygen evolving complex. In: Pecoraro VL (ed) Manganese Redox Enzymes, pp 47–70. VCH, New York

Frasch WD and Mei R (1987) Hydrogen peroxide as an alternate substrate for the oxygen-evolving complex. Biochim Biophys Acta 891: 8–14

Horwitz CP, Winslow PJ, Warden JT and Lisek CA (1993) Reaction of the Schiff-base complexes (X-SALPRN)Mn^{II} [X=H, 5-Cl, 5-CH_3O; SALPRN=1,3-Bis(salicylideneamino)propane] with dioxygen and reactivity of the oxygenated products. Inorg Chem 32: 82–88

Izutsu K (1990) Acid-base dissociation constants in dipolar aprotic solvents, Vol 35. Blackwell Scientific Publications, Brookline Village, MA, 166 pp

Jahns P, Haumann M, Bögershausen O and Junge W (1992) Water oxidation: 1:1:1:1 proton over electron stoichiometry in CAB-protein depleted thylakoids and PS II core particles. In: Murata N (ed) Research in Photosynthesis, Vol II, pp 333–336. Kluwer Academic Publishers, Dordrecht

Jahns P, Lavergne J, Rappaport F and Junge W (1991) Stoichiometry of proton release during photosynthetic water oxidation: A reinterpretation of the responses of neutral red leads to a non-integer pattern. Biochim Biophys Acta 1057: 313–319

Joliot P and Kok B (1975) Oxygen evolution in photosynthesis. In: Govindjee (ed) Bioenergetics of Photosynthesis, pp 388–413. Academic Press, New York

Kolthoff IM, Bruckenstein S, MK and Chantooni J (1961) Acid-base equilibria in acetonitrile. Spectrophotometric and conductometric determination of the dissociation of various acids. J Am Chem Soc 83: 3927–3935

Kristjánsdóttir SS and Norton JR (1992) Acidity of hydrido transition metal complexes in solution. In: Dedieu A (ed) Transition Metal Hydrides, pp 309–359. VCH Publishers, New York

Larson E, Lah MS, Li X, Bonadies JA and Pecoraro VL (1992) Manganese-manganese separations in oxide- and alkoxide-bridged complexes: Correlation of structure with ligand type and number. Inorg Chem 31: 373–378

Larson EJ and Pecoraro VL (1991a) Catalytic disproportionation of hydrogen peroxide by [Mn^{IV}(μ_2-O)(SALPN)]$_2$. J Am Chem Soc 113: 7809–7810

Larson EJ and Pecoraro VL (1991b) The peroxide dependent μ_2-O bond formation of [Mn^{IV}SALPN(O)]$_2$. J Am Chem Soc 113: 3810–3818

Larson EJ, Riggs PJ, Penner-Hahn JE and Pecoraro VL (1992) Protonation of [{Mn^{IV}(saltn)(μ_2-O)}$_2$] results in significant modification of structure and catalase-like activity. J Chem Soc Chem Commun 102–103

Ono T-A, Noguchi T, Inoue Y, Kusunoki M, Matsushita T and Oyanagi H (1992) X-ray detection of the period-four cycling of the manganese cluster in photosynthetic water oxidizing enzyme. Science 258: 1335–1337

Thorp HH, Sarneski JE, Brudvig GW and Crabtree RH (1989) Proton-coupled electron transfer in [(bpy)$_2$Mn(O)$_2$-Mn(bpy)$_2$]$^{3+}$. J Am Chem Soc 111: 9249–9250

Wille B and Lavergne J (1982) Measurement of proton translocation in thylakoids under flashing light using a spin-labelled amine. Photobiochem Photobiophys 4: 131–144