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Manganese-histidine cluster as the functional center of the water oxidation complex in photosynthesis

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Abstract. The recent model of Kambara and Govindjee for water oxidation [Kambara T. and Govindjee (1985) Proc. Natl. Acad. Sci. U.S.A., 82:6119–6123] has been extended in this paper by examining all the data in order to identify the most likely candidate for the 'redox-active ligand' (RAL), suggested to operate between the water oxidizing complex (WOC) and Z, the electron donor to the reaction center P680. We have concluded that a very suitable candidate for RAL is the imidazole moiety of a histidine residue. The electrochemical data available on imidazole derivatives play heavily in this identification of RAL. Thus, we suggest that histidine might play the role of an electron mediator between the WOC and Z. A model of S-states in terms of their plausible chemical identity is presented here.

Abbreviations

J, electronic spin of ion; P680, reaction center chlorophyll; RAL, Redox active ligand; S_n, state of the oxygen-evolving system; WOC, water oxidation complex; Z, electron donor to P680

Introduction

After examining all the data in the literature Kambara and Govindjee [18, 19] have recently proposed a new model for the molecular mechanism of water oxidation in photosynthesis. Various highlights of this new model, to be referred hereafter as the KG model, are schematically indicated in Figure 1. Two pools of manganese ions, each with two manganese ions, were proposed to exist, one of which is located in the hydrophobic cavity in the 'intrinsic' 34kD protein and the other on the hydrophilic surface of the 'extrinsic'

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Dedicated to Prof. L.N.M. Duysens on the occasion of his retirement

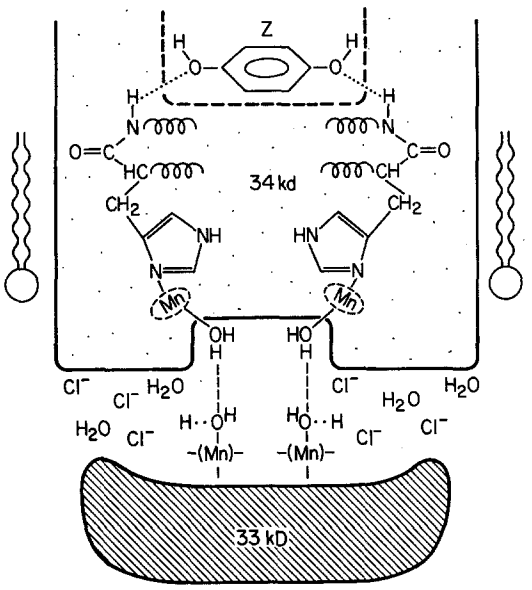

Figure 1. Schematic view of the modified Kambara-Govindjee [19] model for the molecular mechanism of water oxidation in photosynthesis. Two manganese ions, (Mn), are located in a region between the 'extrinsic' 33kD and 'intrinsic' 34kD proteins. Water oxidation occurs at the other two manganese ions [Mn] embedded in the 'intrinsic' protein. The water oxidation is assisted, in our hypothesis, by two redox-active ligands in the form of imidazole moieties.

33kD protein. These two pools of manganese ions are connected by hydrogen bonds through which protons and electrons can be transferred. The oxidation of two water molecules to give one dioxygen molecule is carried out by the two intrinsic manganese ions and protons are transferred from the intrinsic manganese ions to the extrinsic manganese ions. The oxidation state of the intrinsic manganese ions oscillate between Mn(III) and Mn(IV). It was further proposed that electron transfer occurs from this array of manganese ions in the water oxidizing complex (WOC) to Z^+ (Z is a plastoquinol and an electron donor to the reaction center chlorophyll P680). This transfer occurs via a redox active ligand (RAL), one of which is bound to each of two intrinsic manganese ions. Thus, it is two Mn(IV) ions and two RAL^+ that remove four electrons from two H_2O molecules to give one O_2.

One of the features of the KG model, as compared to earlier models [see 13,], is the inclusion of RAL between the manganese center in the WOC and Z. The existence of such an intermediate had also been suggested, among others, by Bouges-Bocquet [5] and by Boska and Sauer [4] on the basis of kinetic analyses. Each RAL serves as a one-electron sink that is intimately involved with one of the two intrinsic manganese ions. Recent work [22] on model manganese complexes has shown that ligands based on o-quinones

can serve as one-electron sinks interacting with manganese ions. When the temperature of a solution containing a manganese complex with two such ligands coordinated to Mn was changed, it was found that each ligand reversibly changes from the 1- to 2-state with a concomitant change in the manganese ion from Mn(II) to Mn(IV). It is thus possible that the p-quinone plastoquinone functions as the RAL, shuttling between the semiquinone(1-) and hydroquinone(2-) forms. However, the reported number of plastoquinone moieties in PSII is about 3 [27, 40] and in view of the other requirements for plastoquinones in the electron-transport chain, there does not seem to be sufficient quantity of plastoquinone present for it to serve as the RAL [19].

In the development of the KG model [19] it was also suggested that aromatic amino acid residues such as histidine and tyrosine could function as the RAL. In this paper we examine this issue in detail and propose histidine as the likely candidate for the RAL. Although the amino acid analysis and sequence of the 'intrinsic' 34kD polypeptide is not yet available [13], the gene mapping data reported by Rasmussen et al. [30] for the membrane D_2 polypeptide of pea chloroplast genome have shown that it is part of the PSII and suggest that it is identical to the 'intrinsic' polypeptide associated with the electron donor of PSII [34]. The remarkable feature of the D_2 polypeptide is that it is rich in histidine residues (7–8 histidines out of 300 residues) and very low in the lysine residues which are found to be abundant in the 'extrinsic' 33kD polypeptide [20].

The suggestion made in this paper that histidine may serve as the RAL moiety which mediates electron transfer between the WOC and Z by interacting with the intrinsic manganese ions is shown to be consistent with the redox-potential requirements of an intermediary between the WOC and Z, the potential ligand capabilities of RAL, and the pH dependence of O_2 evolution. A detailed scheme is proposed to show the functioning of histidine as the RAL as the intrinsic manganese ion pair cycles between the various redox states of the water oxidation complex (i.e., the so-called S_n states). Our expectations as to the EPR signals that should be seen for the different S_n states are discussed.

Histidine as the Redox Active Ligand

The electron mediator between WOC and Z is presently assumed to be a RAL. This RAL might either act as a ligand of the intrinsic manganese ions, or it might just be an one-electron sink that is in proximity to an intrinsic manganese ion, i.e., each RAL might not be directly bonded to a manganese ion. If it is just close to a manganese ion, effective electron flow between the intrinsic manganese ion and the RAL would be possible by a tunneling mechanism.

Catechols have *not* been detected in the PSII. As we indicated above,

there also does *not* seem to be sufficient plastoquinone present for it to be the RAL. Furthermore, the mid-point potentials of various redox couples of catechols and quinones as given by Rich [32] do not support their identification as the RAL, since the potential of RAL/RAL^+ should be between that of H_2O/O_2 ($E_{m,7} = +0.8\,V$) and Z/Z^+ ($E_{m,7} = +1.0\,V$). The only one that has the appropriate potential for placement between the WOC and Z is the $QH_2/QH_2^{\cdot+}$ couple at a potential of $\sim +0.9\,V$. However, in this protonated form plastoquinol would not be expected to be a good ligand for a transition metal ion such as the manganese ion (see [29] and references cited therein). Furthermore, if Z is a bound plastoquinol PQH_2 [28] (perhaps, plastoquinol A [39], it would also not bind directly to the intrinsic manganese ions.

The mediation of electron flow between the WOC and Z by specific amino acid side chains is attractive in light of accumulating data indicating that the binding site of the intrinsic manganese ions is close to hydrophobic polypeptides [7, 25, 42]. It was pointed out by Isied [17] that low lying, empty π^* orbitals in tyrosine or the filled 2p orbitals in histidine can facilitate electron mediation. The formation of a radical cation, i.e., RAL^+, due to transfer of an electron to Z^+, is assumed for the electron mediation by RAL in the KG model [19]. The formation of a radical cation is indeed preferable for these aromatic amino acids, for their oxidation redox potentials are in the range of +0.8 to +1.0 V [26]. This is the desirable range for RAL an electron mediator between the WOC and Z. In this connection, we mention that an intermediate M, suggested by Renger (see e.g. ref. [31]) to have a redox potential in the range of +200 to +400 mV, would not fulfill our criterion for RAL.

There are two important considerations that lead to the choice of histidine as the RAL among all possible amino acid side chains. It has been shown by Brabec and Mornstein [6] that tyrosine and histidine both are electrochemically active. Tyrosine is oxidized at +0.7 V *vs.* SCE, while histidine shows a peak at +1.1 V *vs.* SCE at a graphite electrode. Furthermore, it was shown by coulometric measurements that oxidation of tyrosine involves a two-electron process in which the quinonoidal radical intermediates are not formed. The fact that tyrosine undergoes a two-electron oxidation process at +0.7 V may eliminate it from contention for RAL, because RAL is to serve as a one-electron sink. On the other hand there are precedents in the literature for the formation of radical cations from imidazole or substituted imidazoles [33, 35]. Eaton and Wilson [12] have shown that imidazole ligands can mediate the transfer of electrons to heme proteins by forming a transient radical under mild conditions.

If the RAL needs to be coordinated to the intrinsic manganese ions, then, in comparison to other amino acid residues the imidazole moiety of histidine is particularly well suited for this. For example, it has been shown by several workers (see references cited in [14]) that free tyrosine functions as a bidentate ligand without involving the aromatic hydroxyl group, while free histidine

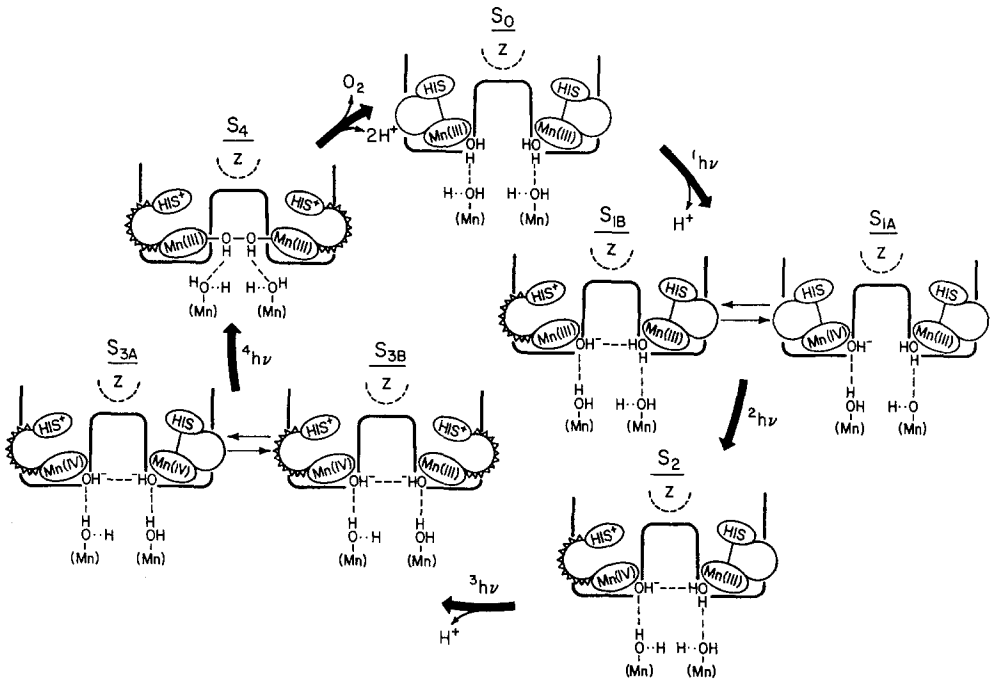

Figure 2. A diagram for the 'Histidine Model' for Kok's S_n states. Oxidation state changes are shown for the 'intrinsic' manganese ions and for the nearby histidine (His) residues. The wavy line connecting a Mn ion and its nearby His symbolically indicates a protein conformation different than is present for the state where a solid line is shown.

exhibits an ambivalent donor character depending upon the pH conditions [24]. At physiological pH in the thylakoid membrane, even though it is part of a polypeptide chain a histidine residue will still be able to interact through one nitrogen of the imidazole moiety. Seela et al. [38] have reported the preparation and characterization of a Mn(III) complex which has a coordinated imidazole ligand. Furthermore, conformational changes in the protein structure could modulate the nature of the interaction between the imidazole nitrogen atom of one RAL and a manganese ion.

Description of the 'Histidine Model'

The present model, which is called the 'histidine model' here, is based upon the KG model [19] for water oxidation in photosynthesis but utilizes the coordination and redox chemistry of histidine to explain the established facts relating to electron transfer from H_2O to Z. The microscopic mechanism of electron transfer and water oxidation in photosynthesis, consistent with Kok's four photon scheme, is shown in Figure 2. Only the two 'intrinsic'

manganese ions are thought to be involved in water oxidation and they are shown as being bound into the 'intrinsic' 34kD protein. The two 'extrinsic' manganese ions are located nearby. These two ions are believed to be Mn(III) ions (each with spin J = 2) which are *not* involved in the redox processes and therefore do not change their oxidation states.

We shall first examine the reactions of the WOC as the latter passes through Kok's S_n states. Absorption of a photon leads to the oxidation of the reaction center P680 to $P680^+$; this is followed by electron flow from Z to $P680^+$ producing Z^+. During the transition of S_o to S_1, Z^+ is reduced by an electron from one of the two histidine-Mn(III) pairs, and a proton, originating in the water molecule bound to this manganese ion, is released. The S_1 state is suggested to exist in two different forms which are in equilibrium. In one form (S_{1B}) the oxidized histidine-manganese pair is described as His^+-Mn(III), whereas in the other it is described as His-Mn(IV). Such an equilibrium involving the shuttling of an electron between a ligand and a manganese ion is well established [22] for manganese complexes with o-quinone-derived ligands. We suggest that the interconversion of S_{1A} and S_{1B} may be triggered by a change in the protein conformation. In fact, it is possible that the imidazole moiety is coordinated to the Mn(IV) ion in S_{1A} and that the conformational change moves the imidazole moiety such that His^+ is not coordinated to the Mn(III) ion in S_{1B}.

During the transition of S_1 to S_2, a second electron is removed from the *same* histidine-manganese pair as in the S_o to S_1 transition. This produces a His^+-Mn(IV) pair.

During the S_2 to S_3 transition, an electron transfers to Z^+ from the second histidine-manganese pair, for it is not possible to oxidize further the first pair beyond His^+-Mn(IV). The S_{3B} state is produced and, in analogy with the $S_{1A} \rightleftharpoons S_{1B}$ equilibrium, there is an equilibrium between the S_{3B} and S_{3A} states. Furthermore, a proton originating in the H_2O bound to the manganese ion at the second histidine-manganese pair is released. Now both intrinsic manganese ions have a OH^- ligand.

During the S_3 to S_4 transition, the second histidine-manganese pair is fully oxidized to His^+-Mn(IV). Although it is obviously difficult to be sure of the order of events, the net result is to form an O–O bond between the two coordinated 'OH^-' ligands. The resulting '$O_2H_2^{2-}$' moiety is then deprotonated, coupled with electrons flowing back to the two His^+-Mn(IV) pairs. With the elimination of one O_2 molecule and two protons, two His-Mn(III) pairs are regenerated. Two H_2O molecules are inserted, with each His-Mn(III) having one H_2O molecule coordinated to it.

Explanation of EPR signals

Finally, it is appropriate to comment on what the EPR signals would be expected to look like for the S states in the present model. It is known that

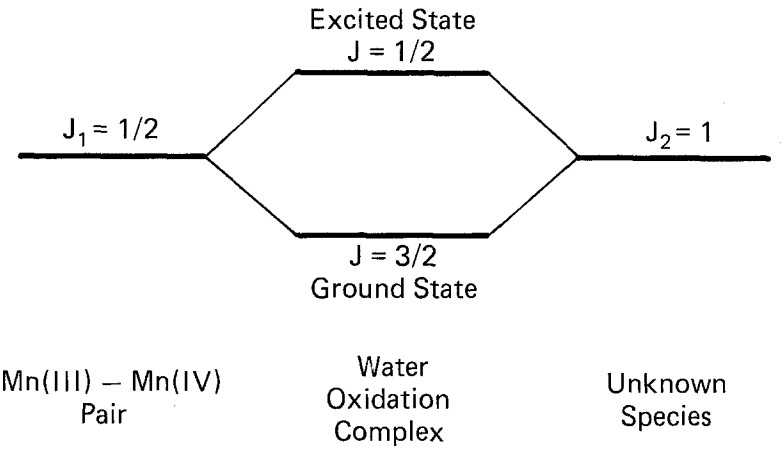

Figure 3. Energy level diagram for the low lying electronic states (J = 3/2 and 1/2) of the Mn(III)-Mn(IV)-(unknown species) complex which corresponds to the water oxidation complex, WOC (center). J_1 is an electronic spin of the antiferromagnetically coupled Mn(III)-Mn(IV) pair, suggested to be the intrinsic Mn pair, and J_2 is an electronic spin of the unknown species, suggested to be the extrinsic Mn(III)-Mn(III) pair.

the manganese complexes in the WOC do not give an EPR signals *in situ* at physiological temperatures [3]. A low-temperature EPR signal for the S_2 state of the WOC has been reported [11, 15], and, on the basis of the magnitude of observed hyperfine structure, the signal was attributed to a binuclear Mn(III)Mn(IV) site [11, 15] or a tetranuclear Mn_3(III)Mn(IV) site [10]. A caveat has been raised [23] about deciding which oxidation states of manganese are present if only the magnitudes of manganese hyperfine interactions are known from EPR simulations. In addition, de Paula and Brudvig [9] reported the continuous power saturation and temperature dependence of three EPR signals (*vide infra*) that are generated by low-temperature illumination of dark-adapted PSII membranes to give the S_2 state. de Paula and Brudvig [9] have concluded that the simplest model which could accommodate the observation of non-Curie type temperature dependence and the power saturation characteristics they observe would be a Mn(III) (electronic spin J = 2)-Mn(IV)-(J = 3/2) pair involved in a relatively strong *antiferromagnetic* exchange interaction. The interaction between Mn(III) and Mn(IV) would give a resultant $J_1 = 1/2$ for the pair (see Figure 3, left). If this Mn(III)-Mn(IV) pair would interact *ferromagnetically* with an unidentified species that has a $J_2 = 1$ state (Figure 3, right), we would obtain two low-energy electronic states of the Mn(III)-Mn(IV)-(unknown species) complex which corresponds to the WOC. One state, the ground state, is characterized by J = 3/2, which simply means that it has three unpaired electrons. The other is an excited electronic state with J = 1/2, which means it has one unpaired electron. If the energy separation between the J = 3/2

and $J = 1/2$ states of this Mn(III)-Mn(IV)-(unknown species) complex is comparable to thermal energies, then the $J = 1/2$ excited state will be populated, according to Boltzman distribution. It is believed [9] that the non-Curie law type EPR signal arises from complexes that are in this $J = 1/2$ state.

Even though the EPR signal observed for the S_2 state is clearly very useful and, in fact, is one of the few ways to directly monitor the electronic structure of the polymanganese WOC, it must be emphasized that very small interaction energies dramatically affect the appearance of an EPR signal [2]. A magnetic exchange interaction between two paramagnetic centers is always propagated by an orbital pathway; however, the distance between the two paramagnetic centers can be quite large, i.e., greater than 10–15Å [16].

The combination of manganese ions and His^+ indicated for the S_2 state in Figure 2 could lead to the type of EPR signals that have been reported seemingly only under one condition. If the His^+ radical was involved in a very weak magnetic exchange interaction with the Mn(IV) ion, then such an EPR signal could result. A diminishingly weak or non-existent exchange interaction could be the result of the His^+ being at an appreciable distance from the Mn(IV) ion, *or* could result from a poor orbital pathway for such an interaction. In this circumstance the two 'intrinsic' manganese ions could be the Mn(III)-Mn(IV) pair that is experiencing a relatively strong antiferromagnetic interaction to give a $J_1 = 1/2$ ground state. The two 'extrinsic' manganese ions form a Mn(III)-Mn(III) pair, which if they are also involved in a somewhat weaker antiferromagnetic interaction, would have a $J = 0$ ground state with a thermally populated (at liquid-helium temperatures) $J_2 = 1$ excited state. The weakly coupled extrinsic Mn(III)-Mn(III) pair corresponds to the unknown species in the model of de Paula and Brudvig [9]. A ferromagnetic interaction between the $J_2 = 1$ excited state of the 'extrinsic' Mn(III)-Mn(III) pair and the $J_1 = 1/2$ ground state of the Mn(III)-Mn(IV) pair would give a $J = 3/2$ ground and $J = 1/2$ excited states for the tetranuclear array as shown in Figure 3. This ferromagnetic interaction between the 'intrinsic' Mn(III)-Mn(IV) pair and the 'extrinsic' Mn(III)-Mn(III) pair could be propagated by the hydrogen bonds pictured in Figure 2. Weak magnetic exchange interactions have been reported [21] to exist between two manganese ions that are connected by hydrogen-bonding contacts.

Objections to the formulation of S_2 state in Figure 2 could be raised by noting that no EPR signal [8] or electronic absorption band [40] corresponding to His^+ have been reported for the S_2 state of the WOC. An organic radical such as His^+ might be expected to give a relatively sharp EPR signal close to $g = 2.0$. However, if His^+ is near to a paramagnetic transition metal center, then the EPR signal for His^+ can be distorted even to the point that it is quite difficult to detect. An example of this type of effect can be seen in the work [1, 36, 37] on horseradish peroxidase compound I (HRP I). HRP I is two oxidizing equivalents above the native Fe(III) state of this heme-protein. It

has been characterized as having Fe(IV) ion bonded to a porphyrin π-cation radical. The early EPR studies [1] of HRP I revealed only minute fractions of an unpaired electron for the porphyrin radical. It has been shown that only if either dispersion-derivative rapid-passage techniques [36] or rapid adiabatic passage conditions [37] are employed to record the EPR can the value of one unpaired-electron per porphyrin be obtained. The influence of the Fe(IV) ion on the porphyrin radical results from a combination of through-space dipole–dipole interaction of the two unpaired-electron centers and a *weak* magnetic exchange interaction between the Fe(IV) ion and the porphyrin radical [37]. Furthermore, in order to simulate the line shape of the porphyrin radical EPR signal, it was necessary to suggest that there is a distribution of magnitude of magnetic exchange interaction present [37].

Thus, in this new model, it is not unreasonable to suggest that a EPR signal for His^+ cannot be easily seen for the S_2 state. In this new model, the EPR signal observed [9, 10, 11, 15] for the S_2 state could be explained by proposing that His^+ is only involved in a *very weak* magnetic exchange interaction with the intrinsic Mn(III)-Mn(IV) pair. This Mn(III)-Mn(IV) pair experiences a relatively strong antiferromagnetic exchange interaction to give a $S = 1/2$ state which is ferromagnetically coupled to the $S = 1$ state of the *extrinsic* Mn(III)-Mn(III) pair. If there is a distribution in the magnitude of the weak magnetic exchange interaction between His^+ and the intrinsic Mn(III)-Mn(IV) pair, then it would take particular care to see the EPR signal for His^+. The distribution in magnitude of exchange interaction could reflect a distribution in relative orientation of the His^+ imidazole moiety relative to the Mn(III)-Mn(IV) pair.

There does not seem to be adequate data available at this time to say why it is apparently not possible to identify an electronic absorption band assignable to His^+ [40, 41]. The present authors are unaware of a study in which the optical band for His^+ as a part of a protein structure has been assigned. Thus, with all the bands seen in the *difference* electronic absorption spectrum for the S_2 state, it is difficult to know whether or not a band for His^+ is seen. In the end, we emphasize that what we have presented here is a reasonable *working hypothesis* that remains to be tested.

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