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# Manganese Compounds as Water Oxidizing Catalysts in Artificial Photosynthesis

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## 1. Introduction

Artificial photosynthesis is an umbrella term but it could be introduced as a research field that attempts to mimic the natural process of photosynthesis and uses sunlight to oxidizing and reducing different compounds. In this process, we could assume water as one of the compounds that could be reduced and (or) oxidized to hydrogen and (or) oxygen, respectively. Water splitting is the general term for a chemical reaction in which water is decomposed to oxygen and hydrogen (Pace, 2005).

Production of hydrogen fuel from electrolysis of water would become a practical strategy if we could find a ''super catalyst'' for water oxidation reaction (Bockris, 1977). Super catalyst means a stable, low cost, efficient and environmentally friendly catalyst. The water oxidation half reaction in water splitting is overwhelmingly rate limiting and needs high over-voltage (~1V) that results the low conversion efficiencies when working at current densities required, also at this high voltage, other chemicals will be oxidized and this would be environmentally unacceptable for large-scale hydrogen production (Bockris, 1977). Thus, a significant challenge in the sustainable hydrogen economy is to design a water oxidizing catalyst.

## 2. Water Oxidizing Catalysts in artificial photosynthesis

In past few years, there has been a tremendous surge in research on the synthesis of various metal compounds aimed at simulating water oxidizing complex (WOC) of photosystem II (PSII) (Liu et al., 2008; Kanan, M.W. & Nocera, 2008; Cady et al., 2008; Yagi & Kaneko, 2001; Ruttinger & Dismukes, 1997). Of these materials, the Co, Ru and Ir compounds have been shown to be an effective catalyst for water oxidation. However, most of the compounds are expensive and often relate to potentially carcinogenic salts.

Particular attention has been given to the manganese compounds aimed at simulating the WOC of PSII (Umena et al., 2011) not only because it has been used by *Nature* to oxidize water but also because manganese is cheap and environmentally friendly. In this chapter we consider manganese compounds as structural or (and)  functional models for the WOC of PSII

### 2.1 Structural models for biological Water Oxidizing Complex

There are many mono, di, tri and tetra nuclear manganese complexes as structural models for the WOC in PSII (Mullins & Pecoraro, 2008).
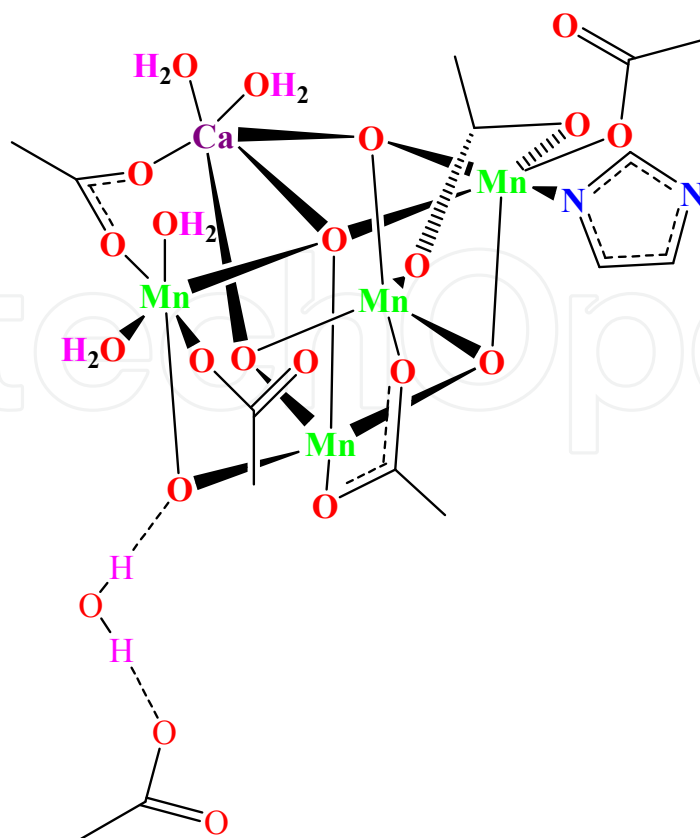
Fig. 1. The WOC and the localization of the substrate water binding sites on the WOC (Umena et al., 2011).

The WOC in PSII is a tetranuclear manganese complex (Fig.1) (Umena et al., 2011). However, mononuclear models are useful and simple complexes for the isolation of high-valent complexes. Regarding these mononuclear manganese complexes, we could obtained many information about spectroscopic properties of Mn(V) compounds as there are no Mn(V) synthetic examples of dinuclear or higher nuclearity structures that have been crystallographically characterized (Fig. 2.) (Mullins & Pecoraro, 2008).

Water and terminal hydroxo ligands in Mn(IV) complexes are very important as there are suggested as one of the substrates for oxygen production in the WOC of PS II. Busch and coworkers reported the first structurally characterized example of a mononuclear Mn (IV) complex with two terminal hydroxo ligands (Fig. 2) (Yin et al., 2006). Using the pH titration of aqueous solutions of the complex, it revealed two acid–base equilibria with $pK_1 = 6.86$ and $pK_2 = 10$, the latter apparently being associated with dimer formation. The complex has shown as a catalyst in olefin epoxidation and hydrogen atom abstraction reactions (Yin et al., 2006).

The Mn(V) = O are very important and it has been proposed as an intermediate in Natural water oxidation. Miller et al have reported the first structurally characterized Mn(V) = O complex (Fig. 2a) (Miller et al., 1998). The complex could not oxidize water but give to us important spectroscopic information of Mn(V) = O group that proposed as an intermediate in biological water oxidation (Miller et al. 1998). However, as considered by Pecoraro, these synthetic Mn(V) = O complexes are stabilized by special ligand(s) and the activity of Mn(V) = O could be completely different from Mn(V) = O of the WOC in PSII (Mullins & Pecoraro, 2008).
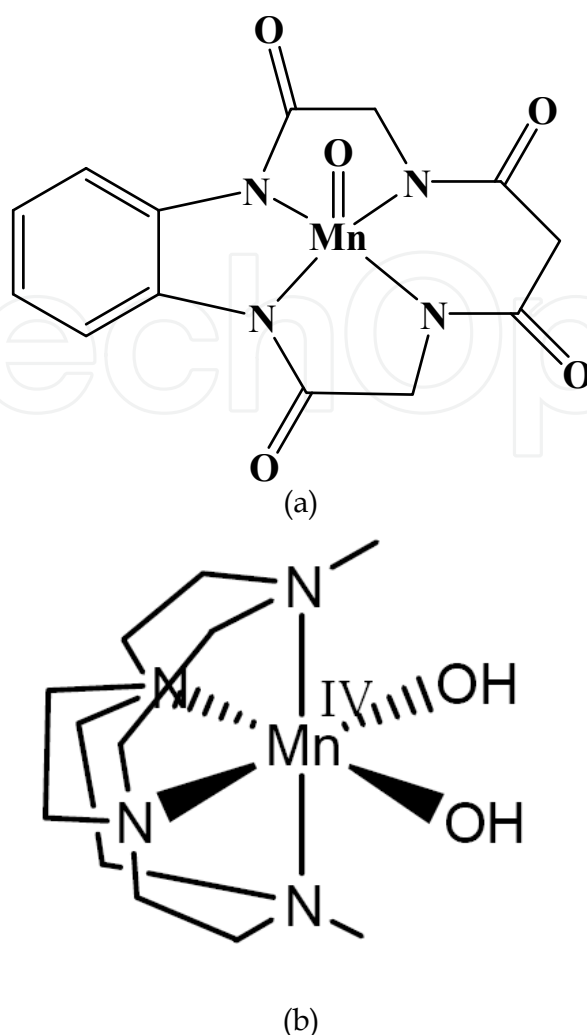
(a)



(b)

Fig. 2. Schematic structures of a mononuclear Mn(V) (Miller et al., 1998) (a) and a Mn(IV) complex terminal hydroxo ligands (b) (Yin et al., 2006).

Many dinuclear manganese complexes have been studied with different oxo bridge (μ-O) as possible models for the WOC. The relationship between Mn-Mn distance and Mn–O–Mn angle has been considered for such complexes (Mullins & Pecoraro, 2008).

In 1988, there was suggestion that WOC had a mononuclear manganes center in close proximity to a trinuclear center and this suggestion was emerged basedon magnetic, spectroscopic, and crystallographic studies in 2000 (Mullins & Pecoraro, 2008). Regarding this issue, study of magnetic, spectroscopic, and crystallographic properties of trinuclear clusters has re-emerged and many trinuclear manganese complexes with linear or bent structure and different oxidation states for manganese ions have been synthesized and characterized (Mullins & Pecoraro, 2008).

Tetra nuclear manganese complexes are very interesting group of complexes as they could be studied as structural models for the WOC. These complexes show different structures regarding manganese ions from linear to cubane (Mullins & Pecoraro, 2008) (Fig. 3).

In 2005, Christou and co-workers have reported the first high oxidation state manganese–calcium cluster. The structure contains $[Mn_4CaO_4]$ sub-units similar to that found in the WOC in PSII (Fig. 4) (Mishra et al., 2005). Recently, Kotzabasaki et al. (2011) synthesized a heterometallic polymeric complex $\{[Mn^{III}_6Ca_2O_2(Me\text{-}saO)_6(prop)_6(H_2O)_2].2MeCN.0.95H_2O\}_n$

(prop = propionate; Me-saOH$_2$ = 2-hydroxyphenylethanone oxime) (Fig. 4). Nayak et al. (2011) have also synthesized two new polynuclear heterometallic cluster complexes with [Mn$^{III}$3M$^{II}$Na] (M= Mn, Ca) core were synthesized using two in situ formed Schiff bases. This compound appeared to catalyse water oxidation in the presence of NaOCl which was followed by using Clark electrode and online mass spectrometry (Nayak et al., 2011).
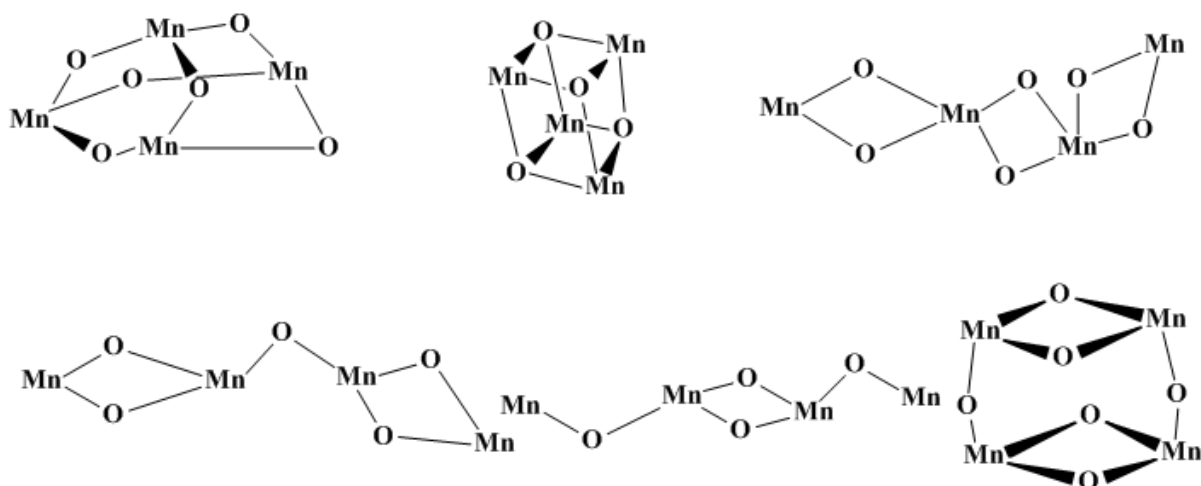


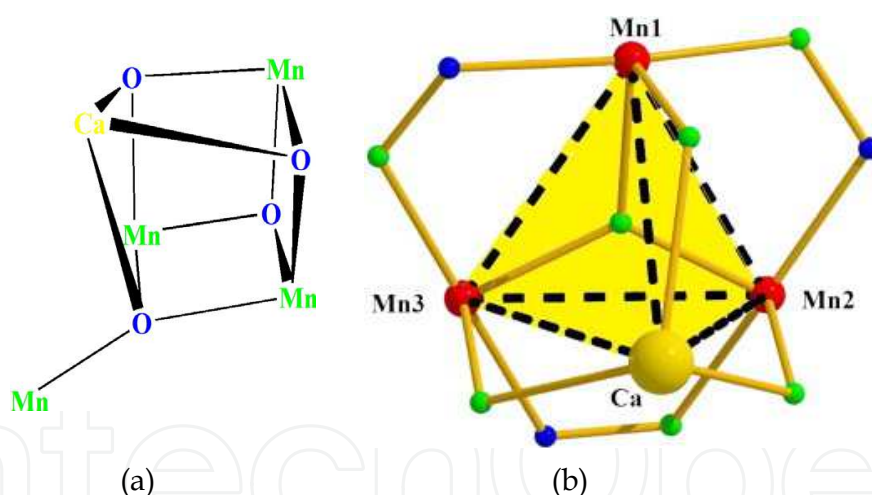Fig. 3. Different core types observed in Mn-oxo tetramers.



(a)                                                    (b)

Fig. 4. The first high oxidation state manganese–calcium cluster reported by Christou and co-workers. The structure contains [Mn$_4$CaO$_4$] sub-units similar to that found in the WOC in PSII (a). The heterometallic polymeric complex {[Mn$^{III}$$_6$Ca$_2$O$_2$(MesaO)$_6$(prop)$_6$(H$_2$O)$_2$]·2MeCN·0.95H$_2$O}$_n$ reported by Kotzabasaki et al. (2011) (b) (figure was reproduced from Kotzabasaki et al. (2011)).

In 1997, Styring's group reported a molecule containing a sensitizer covalently linked to a manganese complex (Fig. 5). In this compound, the ruthenium chromophore could donate an electron to an external acceptor and consequently oxidize a coordinated manganese ion with rate constants ~ 50 ns to 10 μs. Then this group showed that how a Ru–Tyr molecular dyad could be used to power the light driven oxidation of a dinuclear Mn$_2$$^{III,III}$ complex (Lomoth et al., 2006). Similar to PSII, it was shown that upon light absorption, a chain

reaction of first electron transfer could be achieved whereby the Ru(III) species, obtained in presence of an electron acceptor, was quenched through an intermolecular electron transfer leading to the formation of the tyrosyl radical.
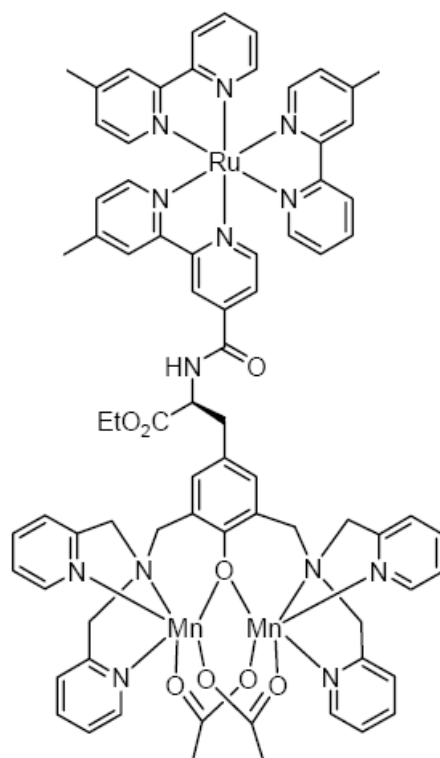


Fig. 5. Molecule containing a sensitizer covalently linked to a manganese complex.

## 2.2 Functional models for biological Water Oxidizing Complex

There are a few manganese complexes that produce oxygen in the presence of different oxidants (Cady et al., 2008; Yagi & Kaneko, 2001; Ruttinger & Dismukes 1997). It is important to know that even if the oxidants may do donate O-atoms that end up in the product oxygen, can nevertheless play an important role in identifying potentially useful catalytic components for water photolysis and electrolysis.

### 2.2.1 Terpy and bpy manganese complexes

It is shown that $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3+}$ and $[(OH_2)(terpy)Mn^{III}(\mu\text{-}O)_2Mn^{IV}(terpy)(OH_2)]^{3+}$ (bpy: 2,2'-Bipyridine; terpy: 2,2';6',2"-terpyridine) (Tagore et al., 2008; Yagi & Narita, 2004) have water oxidation activity in the presence of $(NH_4)_2[(Ce(NO_3)_6]$, NaClO and $KHSO_5$. Yagi and Narita (2004) observed when comparable amount of $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3+}$ or $[(OH_2)(terpy)Mn^{III}(\mu\text{-}O)_2Mn^{IV}(terpy)(OH_2)]^{3+}$ were adsorbed onto Kaolin clay, the addition of a large excess of $(NH_4)_2[(Ce(NO_3)_6]$ to its aqueous suspension produced a significant amount of oxygen. The rate of oxygen evolution increased linearly with the amount of $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3+}$ indicating unimolecular oxygen evolution in contrast with bimolecular catalysis of $[(OH_2)(terpy)Mn^{III}(\mu\text{-}O)_2 Mn^{IV}(terpy)(OH_2)]^{3+}$.

The unimolecular oxygen evolution might be explained by either O-O coupling of di-$\mu$-O bridges or attack of outer-sphere water onto a $\mu$-O bridge in high oxidation species, probably including $\mu$-O$^-$ radical bridges (Yagi & Narita, 2004). When $[(bpy)_2Mn^{III}(\mu\text{-}O)_2Mn^{IV}(bpy)_2]^{3+}$ was dissolved in water containing excess $(NH_4)_2[(Ce(NO_3)_6]$, no evolution of gas was observed, and analysis of the gas phase confirmed that no oxygen was formed; however oxygen evolution was observed when these complex as a solid was added to a $(NH_4)_2[(Ce(NO_3)_6]$ solution (Yagi & Narita, 2004). Isotopic labeling of the solvent water showed that indeed water was oxidized (Yagi & Narita, 2004). It was also reported that $[(OH_2)(terpy)Mn^{III}(\mu\text{-}O)_2Mn^{IV}(terpy)(OH_2)]^{3+}$ has oxygen evolution activity in the presene of $KHSO_5$ or NaOCl, as primary oxidants. A proposal mechanism was reported by Brudvig group for the reaction (Fig. 6) (Cady et al., 2008). Recently, Brudvig's group have reported the attachment of $[(OH_2)(terpy)Mn^{III}(\mu\text{-}O)_2Mn^{IV}(terpy)(OH_2)]^{3+}$ onto TiO$_2$ nanoparticles via direct adsorption. The resulting surface complexes were characterized by EPR and UV-visible spectroscopy, electrochemical measurements and computational modeling. Their results showed that the complex attaches to near-amorphous TiO$_2$ by substituting one of its water ligands by the TiO$_2$, as suggested by EPR data (Li et al. 2009).
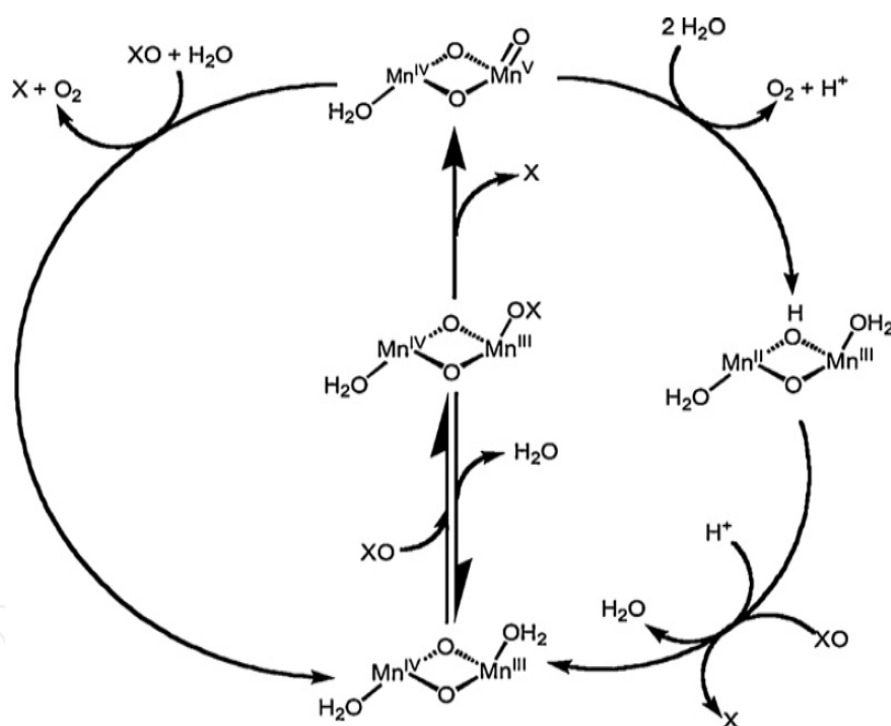


Fig. 6. Schematic diagram of the proposed mechanism of water oxidation by $[(OH_2)(terpy)Mn^{III}(\mu\text{-}O)_2Mn^{IV}(terpy)(OH_2)]^{3+}$ (figure was reproduced from Cady et al. (2008)).

### 2.2.2 Schiff base complex

A number of manganese (III) complexes of the type $[\{MnL(H_2O)\}]^{2+}$ (L = dianion of O,N,tetradentate Schiff base), in aqueous solution, have been shown to liberate dioxygen and reduce p-benzoquinone to hydroquinone when irradiated with visible light (Ashmawy et al., 1985). The photoactivity is critically dependent on the structure of the ligand, the complex $[\{Mn(salpd)(H_2O)\}][ClO_4]$, (salpd = propane-l,3-diylbis(salicylideneiminate)) being the most

active (Ashmawy et al., 1985). All the active complexes exhibit a band at 590 nm in the electronic spectrum, which is absent for the inactive complexes (Ashmawy et al., 1985). The rate of dioxygen evolution is dependent on the manganese (III) complex (first order) and quinone concentrations (order, 0.5) and the pH of the reaction medium, but is independent of solvent. The activation energy for dioxygen evolution in [{Mn(salpd) (H$_2$O)}][ClO$_4$], is 80 kJ mol$^{-1}$, and the evidence points to homolytic, rather than heterolytic, fission of water (Ashmawy et al., 1985). The wavelength dependence of the reaction rate shows a maximum for photolysis in the 450-600 nm region where the quinone does not absorbed (proposal mechanism is shown in Fig. 7) (Ashmawy et al., 1985).
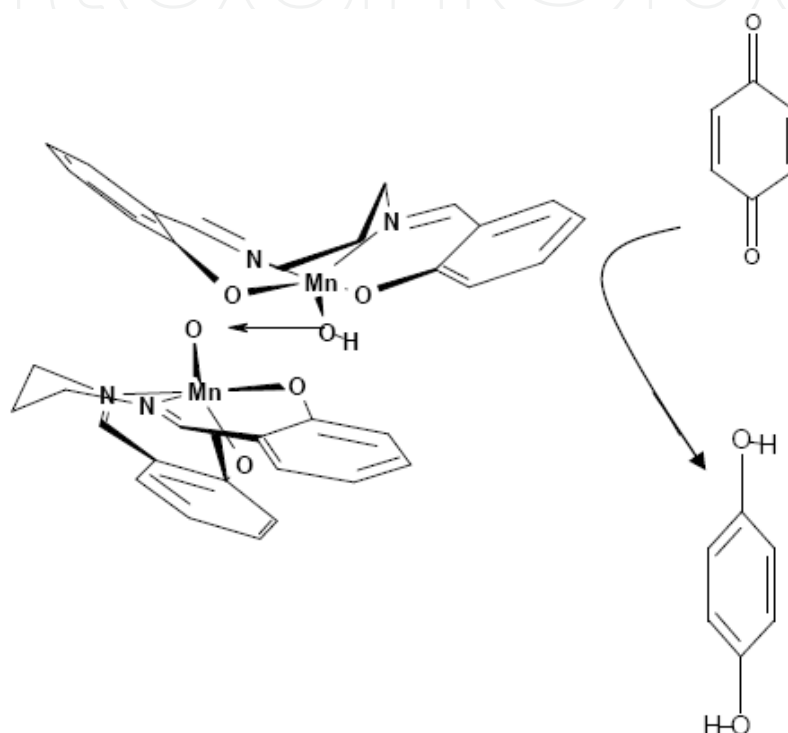


Fig. 7. Proposal mechanism for water oxidation by reduce p-benzoquinone to Hydroquinone (Ashmawy et al., 1985).

Oxygen evolution was also observed upon mixing solid manganese(III) bidentate Schiff base complexes with aqueous solutions of (NH$_4$)$_2$[(Ce(NO$_3$)$_6$] (Najafpour & Boghaei, 2009). However, oxygen evolution was not observed upon mixing solutions of the complexes (in acetonitrile) with Ce(IV). Electron-withdrawing substituents on the Schiff base ligands (NO$_2$, Br) enhanced the reactivity of the manganese complexes toward oxygen evolution. Oxygen evolution was also affected by R groups on the ligands, in the order Me>Et > Bz (Najafpour & Boghaei, 2009).

It was reported that hydrogen peroxide was produced when HClO$_4$ was added in stoichiometric amounts to solutions of the Mn(IV) Schiff base dimer [Mn$_2$(IV)(BuSalen)$_2$(O)$_2$], H$_2$O in acetone at 0 °C (Fig. 8) (Boucher & Coe 1975). The complex was converted in 62% yield to the Mn(III) monomer from which the dimer was initially synthesized by air oxidation in chloroform solution. However, Pecoraro suggested that as [Mn$_2^{IV}$(BuSalen)$_2$(O)$_2$], H$_2$O has catalase activity, if hydrogen peroxide was produced, dioxygen would evolve from solution (Pecoraro et al, 1994).
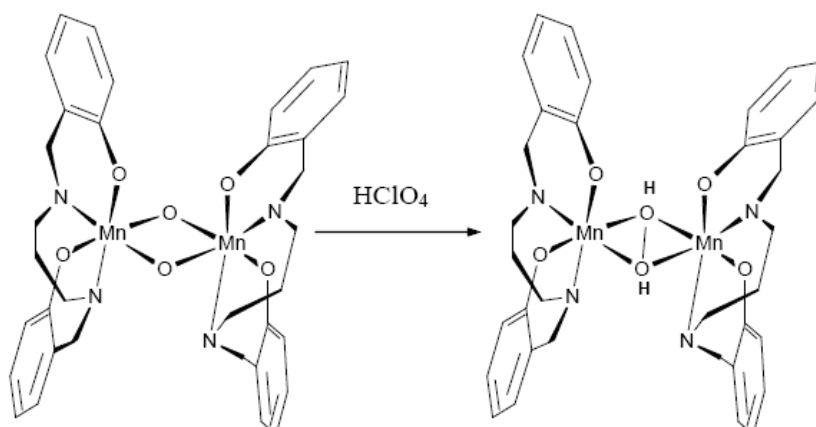
Fig. 8. Proposal mechanism for hydrogen peroxide producing when HClO$_4$ was added in stoichiometric amounts to solutions of the Mn(IV) Schiff base dimmer (Boucher & Coe 1975).

Fujiwara et al. have reported the preparation and characterization of a series of dichloromanganese (IV) Schiff base complexes (Fujiwara et al., 1985). They have shown that the manganese(IV) complex dichlorobis(N-R-3-nitrosalicylideneaminato) manganese(IV) reacts with water to liberate molecular oxygen (Fig. 9) (Fujiwara et al., 1985).
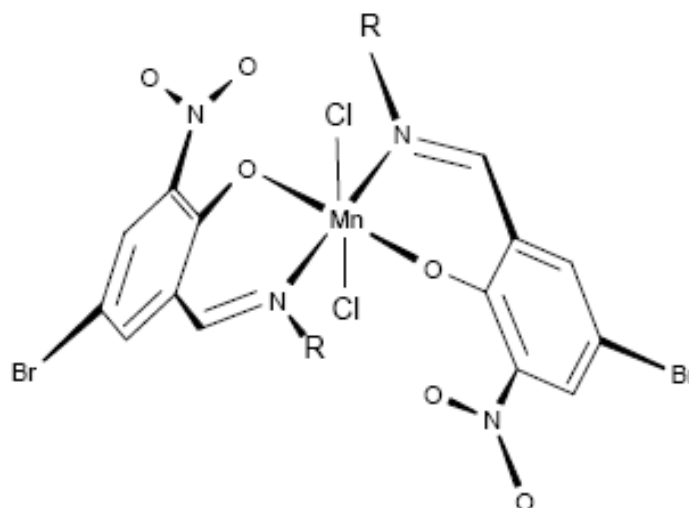


Fig. 9. Structure of the complex *trans*-Mn(IV)L$_2$Cl$_2$ (L = *N*-alkyl-3-nitrosalicylimide) (Fujiwara et al., 1985).

Absorbed spectrometry using an alkaline pyrogallol solution and measurement of dissolved oxygen by an oxygen electrode were employed to detect and determine dioxygen liberated during the reaction of manganese(IV) complexes with water (Fujiwara et al., 1985). It could be seen that the reactivity is affected by the alkyl groups of the complexes: the reaction with water is retarded in order of (mol of O$_2$ per mol of complex) n-C$_3$H$_7$ (0.27)< n-C$_8$H$_{17}$ (0.2)< n-C$_{12}$H$_{25}$ (0.12). These results indicate that the long-chain alkyl groups such as n-C$_8$H$_{17}$ and n-C$_{12}$H$_{25}$ can protect the central manganese(IV) ion from attack by water molecules (Fujiwara et al., 1985). This may arise from hydrophobicity of these groups. In other words, the reactivity of the manganese(IV) complexes with water can be controlled by the choice of alkyl groups. Also they have found that the pH values of reaction decrease in the course of the reaction of the manganese(IV) complexes in the presence of water (without any buffer

solution) (Fujiwara et al., 1985). Using ^{18}O-labeled water showed that indeed water was oxidized in this reaction (Fujiwara et al., 1985).

### 2.2.3 Porphyrin complexes

Shimazaki et al. (2004) have reported dimanganese complexes of dimeric tetraarylporphyrins linked by 1,2-phenylene bridge (Fig. 10). The catalyst can oxidize olefins such as cyclooctene to form epoxide with stiochiometric amount of m-chloroperbenzoic acid. It is proposed that the oxidation of a dimanganese (III) tetraarylporphyrin dimer could give the corresponding high valent Mn(V)=O complex, which is the active species in these oxidation. They reported on the oxidation of the dimanganese porphyrin dimer by employing meta-Chloroperoxybenzoic acid as an oxidant, and the characterization of the resulting Mn(V)=O species by spectroscopic methods.

Furthermore, oxygen evolution was observed from the Mn(V)=O species when a small excess of trifluoromethanesulfonic acid was added (Shimazaki et al., 2004). Mn(V)=O was detected by EPR, UV/VIS, and Raman spectrum (Shimazaki et al., 2004).
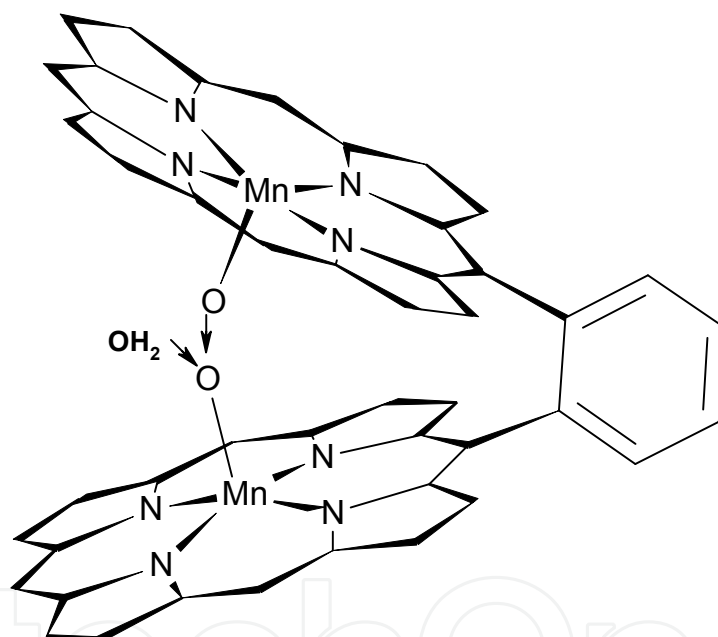


Fig. 10. Dimeric tetraarylporphyrins linked by 1,2-phenylene bridge as a model for the WOC in PSII (Shimazaki et al., 2004).

### 2.2.4 Cubane like model

Several types of experimental evidence have demonstrated that the synthetic complexes $Mn_4O_4(O_2PR_2)_6$, R = Ph and 4–MePh, containing the $[Mn_4O_4]^{6+}$ core surrounded by six facially bridging bidentate phosphinate anions, produce dioxygen following removal of one phosphinate ligand to form the reactive butterfly complex $[Mn_4O_4(O_2PR_2)_5]$ (Fig. 11) (Maniero et al., 2003).

Dissociation of a phosphinate ligand is achieved using light absorbed by a charge transfer O-Mn transition, producing dioxygen in high quantum high yield (46–100%) (Maniero et al., 2003).

The redox potential of $[Mn_4O_4(O_2PR_2)_6]/[Mn_4O_4(O_2PR_2)_6]^+$ is 1.38 V vs NHE, which is considerably greater than those found for the dimanganese(III,IV)/(III,III) couple and the majority of known (IV,IV)/(III,IV) couples. The $[Mn_4O_4(O_2PR_2)_6]$ cubane complex reacted with the hydrogen-atom donor, phenothiazine in a $CH_2Cl_2$ solution, forming $[Mn_4O_4(O_2PR_2)_6]$ and $[Mn_4O_4(O_2PR_2)_6]^+$ as well as releasing two water molecules from the core. This result shows that two of the corner oxos of the cubane can be converted into two labile water molecules. The evolution of oxygen molecule from $Mn_4O_4$ cubane core was corroborated by the detection of $^{18}O_2$ from $[Mn_4O_4(O_2PR_2)_6]$ (Maniero et al., 2003).
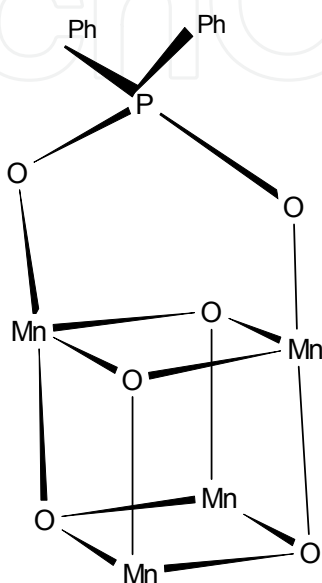


Fig. 11. Synthetic complexes $Mn_4O_4$ $(O_2PR_2)_6$, R = Ph and 4–MePh (only one $O_2PR_2$ is shown).

### 2.2.5 Mn(II) complexes of monoanionic pentadentate ligands

McKenzie's group (Seidler-Egdal et. al., 2011) reported that tert-Butyl hydroperoxide oxidation of Mn(II) complexes of **1** (Fig. 12), in large excesses of the tert-Butyl hydroperoxide,
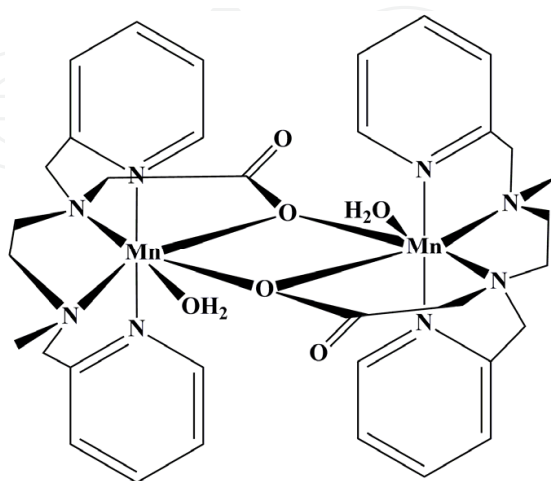


Fig. 12. The Mn(II) complex (**1**) of monoanionic pentadentate ligands reported by McKenzie's group.

is concurrent with an oxygen evolution with turnovers of up to $10^4$ mol of oxygen per mol of [Mn] and calculated rate constants from two series of experiments of 0.039 and 0.026 mol [$O_2$] s$^{-1}$ M$^{-2}$. A 1:1 reaction of tert-Butyl hydroperoxide with [Mn] is rate determining and the resultant species is proposed to be the mononuclear, catalytically competent, Mn(IV)=O (Seidler-Egdal et. al., 2011).

### 2.2.6 Manganese Oxides and Hydroxides

Oxides and Hydroxides of transition metals cations like Fe(III), Co(III), Mn(III), Ru(IV), and Ir(IV) appear to be efficient catalysts for water oxidation in the presence of Ce(IV), $S_2O_8^{-2}$ and Fe(bpy)$_3^{3+}$ as oxidants.

Shilov and Shafirovich in 1965 have shown that colloidal $MnO_2$ catalyzes the oxidation of water to dioxygen in the presence of strong oxidants like Ce(IV) and Ru(bpy)$_3^{3+}$) (Shilov & Shafirovich, 1979 (translation)). Suggested mechanism is shown in Scheme 1.
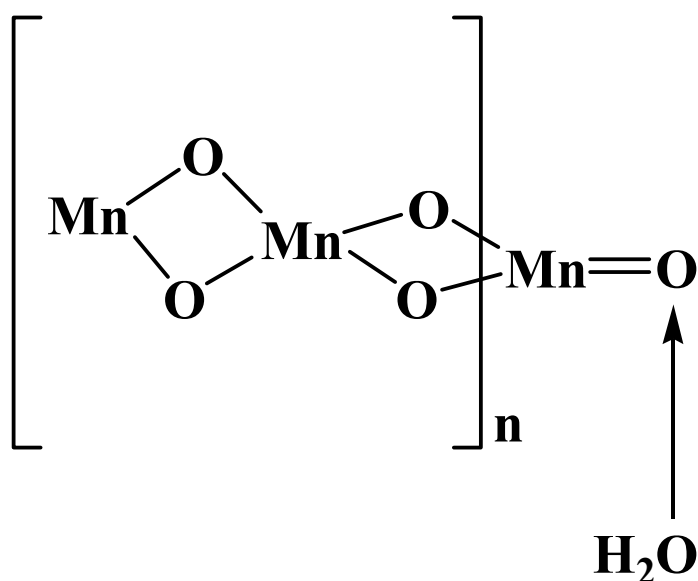


Scheme 1. Suggested mechanism for water oxidation by Oxides and Hydroxides of transition metals.

Recently, we introduced amorphous calcium - manganese oxide as efficient and biomimetic catalysts for water oxidation (Najafpour et al., 2010). These oxides are very closely related to the WOC in PSII not only because of similarity in the elemental composition and oxidation number of manganese ions but also because of similarity of structure and function (Najafpour 2011a,b; Zaharieva et al., 2011) (Fig. 13).

The structure of these amorphous powders have been evaluated, using extended-range X-ray absorption spectroscopy (XAS), X-ray absorption near-edge structure (XANES) and Extended X-Ray Absorption Fine Structure (EXAFS) (Zaharieva et al., 2011). These results reveal similarities between the amorphous powders and the water oxidizing complex of PSII. Two different Ca-containing motifs were identified in these amorphous manganese – calcium oxides (Zaharieva et al., 2011). One of them results in the formation of Mn$_3$Ca cubes, as also proposed for the WOC of PSII. Other calcium ions likely interconnect oxide-layer fragments. It was concluded that these readily synthesized manganese-calcium oxides are the closest structural and functional analogs to the native the WOC of PSII found so far
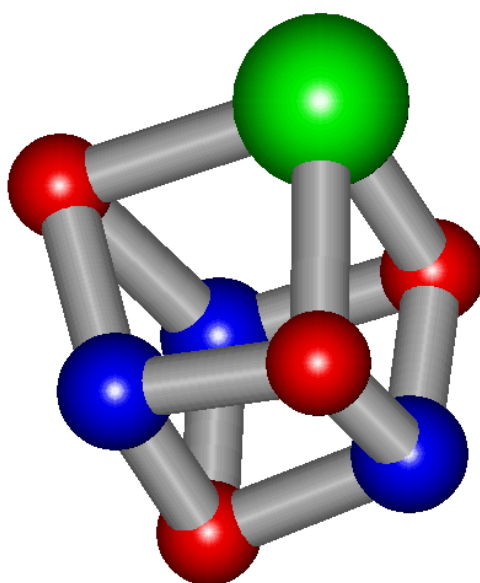
Fig. 13. Motif of edge-sharing $MnO_6$ octahedra (di-μ-oxido bridging) in the manganese – calcium oxides (manganese: blue, oxygen: red and calcium: green) (Zaharieva et al., 2011).

(Zaharieva et al., 2011). Oxygen evolution formation pathways indicated by ^{18}O-labelling studies showed that water oxidation by these layer manganese oxides in presence of cerium (IV) ammonium or $[Ru(bpy)_3]^{+3}$ is a "real" water oxidation reaction and both oxygen atoms of formed dioxygen molecules originated from water (Shevela et al., 2011). In continuation of our efforts to synthesize an efficient and biomimetic catalyst for water oxidation, we synthesized nano - size amorphous calcium - manganese oxides that are very closely related to the WOC in PSII not only because of similarity in the elemental composition, oxidation number of manganese ions and similarity of structure and function to $Mn_4O_5Ca$ cluster in PSII but also because of nearer on the of catalyst particle size as compared to previously reported micro - size amorphous calcium manganese oxides (Fig. 14.).

### 2.2.7 Genetic engineering models

Wydrzynski and co-workers, in a different approach, introduced a reverse engineering approach to build a simple, light-driven photo-catalyst based on the organization and function of the donor side of the PSII reaction centre and a bacterioferretin molecule is being 'coaxed' using genetic engineering to include the chromophores for light absorption and Mn complexes for water oxidation; they could observed oxidation of manganese in this engineered system (Conlan et al., 2007). Recently, Nam and co-workers imtroduced a biologically templated nanostructure for visible light driven water oxidation that uses a genetically engineered virus scaffold to mediate the co-assembly of zinc porphyrins (photosensitizer) and iridium oxide clusters (water oxidizing catalyst) (Nam et al., 2010). Their results suggested that the biotemplated nanoscale assembly of functional components is a promising route to improved photocatalytic water-splitting systems.
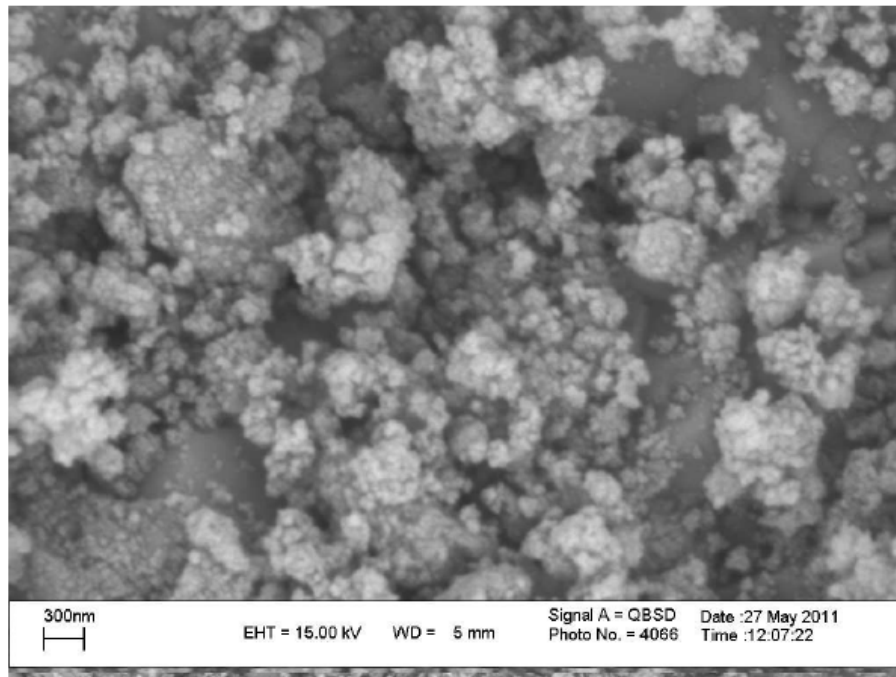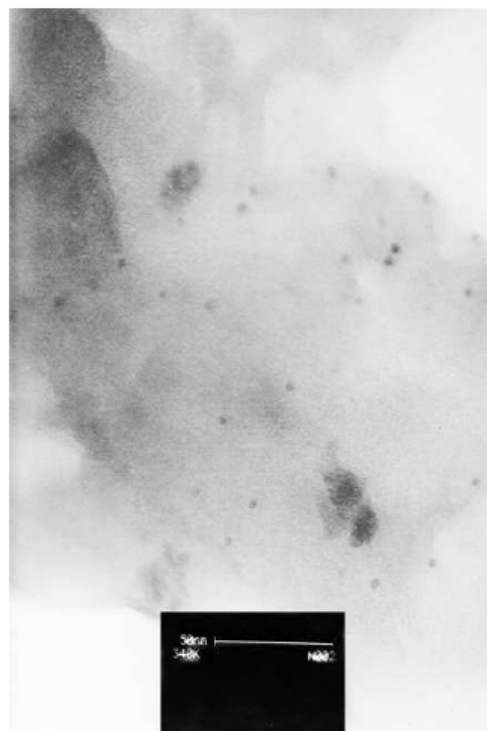
Fig. 14. Scanning electron microscope (SEM) (a) and transmission electron microscopy (TEM) (b,c) images of amorphous calcium - manganese oxides. These readily synthesized manganese-calcium oxides are the closest structural and functional analogs to the native the WOC of PSII found so far.

## 3. Acknowledgment

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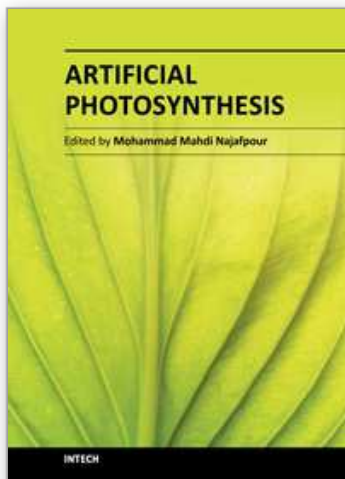
**Artificial Photosynthesis**

Edited by Dr Mohammad Najafpour

Photosynthesis is one of the most important reactions on Earth, and it is a scientific field that is intrinsically interdisciplinary, with many research groups examining it. We could learn many strategies from photosynthesis and can apply these strategies in artificial photosynthesis. Artificial photosynthesis is a research field that attempts to replicate the natural process of photosynthesis. The goal of artificial photosynthesis is to use the energy of the sun to make different useful material or high-energy chemicals for energy production. This book is aimed at providing fundamental and applied aspects of artificial photosynthesis. In each section, important topics in the subject are discussed and reviewed by experts.

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