A Selective Review on Synthetic Oxo - Bridged Polynuclear High - Valent Manganese Centers related to Oxygen Evolving Complex of Photosynthesis

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Abstract: The oxygen - evolving complex (OEC) oxidises water to molecular dioxygen in photosystem II (PS II) at the redox catalytic centre on the lumenal side of PS II, which includes four manganese ions, a calcium ion and a chloride ion. Exact structure or mechanistic pathways charge transfer inside of OEC is still subject to research. Many inorganic complexes have been synthesised which show structural or functional resemblance with OEC. Theses complexes helps us in understanding election transfer mechanisms operating in different steps of the oxygen - evolving complex.

Keywords: Oxygen - evolving complex. Photosynthesis, oxo - bridge, Manganese

1. Introduction

Oxo - bridged polynuclear manganese clusters are very common as an active site of numerous biological redox active enzymes. Catalytic redox centre of several enzymes like superoxide dismutase, catalase and the oxygen evolving complex of photosystem II (PS II) contains Mn. These enzymes are frequently studied by using model complexes that provide information on the nature and reactivity of the active site and about possible reaction mechanisms. Based on these enzymes and on the related model complexes various catalysts have been designed.

The recognisation of these Mn - oxo proteins as a separate class has simulated efforts on the part of inorganic chemists to prepare and characterise model compounds that replicate the physical properties and functions of the polymetallic protein cores. As a consequence, a variety of oxo - bridge di - , tri - and tetramanganese aggregates have been synthesized. These novel molecules promise not only to provide insight in Mn - proteins, but also to serve as a focal point for developing new strategies for the treatment of manganese - related diseases, and for building links between the chemistry of the biosphere and geosphere. Starting from early days enormous number of Mn - complexes have been synthesised and extensively studied depending on their relevance as model complexes or intermediates in the catalytic cycles of OEC.

Oxygen evolving Complex

Photosynthetic water oxidation proceeds at a tetranuclear Mn_4 complex bound to the luminal side of the D_1 subunit of photosystem II (PS II) found in the thylakoid membrances of higher plants, green algae and cyanobacteria. During this process of fundamental importance, which involves the oxidation of two bound water molecules, the dioxygen of the atmosphere is produced as a byproduct.

 $2H_2O \longrightarrow O_2 + 4e^- + 4H^+(1)$

X - ray crystallographic and advanced spectroscopic studies revealed that the catalytic site consist of cluster of four Mn atom and one Ca atom (Mn₄Ca) connected by mono - μ - oxo, di - μ - oxo and or hydroxo bridges and a redox active tyrosine (Y_z), which are specially bound to the protein scaffold that comprised the core of PSII. In addition, Cl - and bicarbonate ion are present as cofactor for water oxidation collectively, this functional unit is referred to as the oxygen evolving complex (OEC). Despite an apparent wealth of information, the exact organization of the Mn₄Ca cluster and the mechanism of O–O bond formation is still not known and is the subject of intense debate.

The OEC is successively oxidised in one - electron steps to yield four equivalents electrons that are used as reducing equivalents. Most, if not all, of these oxidations occur on the tetranuclear core of manganese ions. After the fourth oxidation, a molecule of dioxygen is released and the OEC returns to a lower overall oxidation state. The cycle was established by periodic bursts of dioxygen that occurred with every fourth flash of light given to preparations of photosynthetic centres by Kok (1) in the early 1970's and has been named the S - state cycle (shown in Scheme 1), which proceeds from S₀ to S₄.



Scheme 1

Kok cycle describing photosynthetic water oxidation. For simplicity deprotonation reactions are not shown. Each electron drawn from the OEC is transferred via a redox active tyrosine (Y_z) residue to an oxidized chlorophyll molecule that was excited and oxidised by absorbed light

energy. The electron that had been lost from the chlorophyll then goes on to be utilized as a reducing equivalent further along the line in the photosynthetic system. Many recent studies show that the coupling of electron and proton transfer plays a pivotal role in the process of water splitting. In this regard the functions of Y_z and the protein matrix are still under investigation.

Oxo - bridge Mn in chemistry

High - valent Mn - oxo species are believed to be actively involved in the water oxidation catalytic cycle. This has been determined by extensive EPR and EXAFS studies, as discussed above. Consequently, much effort has been devoted to isolate Mn - oxo complexes with different nuclearities, aided by various chelating (N and/or O donors) ligands. The complexes synthesised have been invaluable in interpreting data obtained for PS II. From the synthetic studies it has been realized that the manganese ions in the +3 (d^4) and +4 (d^3) oxidation states in polynuclear manganese complexes are primarily stabilised with bridging oxide (O^{2 -)} groups. The presence of suitable chelating ligands plays a very important role in the formation of clusters of different nuclearity, a process that is often determined by the thermodynamic stability of the final products. However, it should be pointed out that in many cases the true thermodynamic end point would result in the formation of insoluble extended oxides. Additionally, carboxylate ligands in various bridging modes and halide ions have been employed to provide coordination to the metal centers because of their biological relevance. The spontaneous self assembly approach has long been utilised in the formation of high - valent manganese - oxo complexes. Readily available Mn (II) starting materials can be oxidised in the presence of suitable reagents, such as bromine water, iodine, Ce (IV), iodosobenzene, peroxides, HClO₄, bromate, and also NaOH, to form high - valent Mn species. Aerial oxidation of Mn -(II) precursors has also been reported for the same purpose. Many syntheses have also employed Mn (III) starting materials to prepare high - valent clusters. Permanganate salts, which contain the Mn^{VII} ion, have been used extensively in delivering oxidising equivalents and oxo ligands. The presence of permanganate in these reactions serves a dual purpose, as an oxidant as well as providing another source of Mn ions. A very common reaction pathway to high - valent manganese clusters involves the comproportionation reaction between Mn^{II} and Mn^{VII} ion sources. Potassium or sodium salts of permanganate are used for the reactions done in aqueous medium, whereas tetraalkylammonium salts are used for reactions conducted in organic solvents. Several Mn - oxo species have also been synthesized via bulk electrolysis, ligand substitution, and hydrolyticpathways. The ancillary N - donor and O - donor ligands perform a critical role in the formation and stabilization of oxomanganese clusters. Limitation of aggregation is a key attribute to consider when selecting a ligand. A large number of ligands ranging from bidentate to tridentate to template polydentates that include aliphatic, cyclic, polypyridyl, and Schiff bases have been employed for this purpose. Upon coordination to the metal centers, these ligands usually form stable five - membered and also six - membered chelate rings that in part determine the stability of the complexes.

In the beginning of the study of OEC, a dinuclear mixed valent oxo - bridge unit [(bipy) 2Mn^{III}O2Mn^{IV} (bipy) 2]³⁺ was the key model, obtained by Nyholm and Turc (2) in 1960 and structurally characterised by Plaskin (3) et al. This system has been studied in detail by Calvin et al. (4) This complex in a good EPR model for S₂ state of OEC. In 1986 Brudvig and Crabtree published a mechanistic proposal, based on structurally characterised Mn complexes, followed by shortly there after by a proposal by Vincent and Christou in 1987. (5) The mechanism are based partially on experimental structures, like the known (Mn_6O_6) adamantine type, (Mn_4O_3Y) cubane type, (Mn_4O_2) butterfly type Mn_4 cores. They share the ideas of incorporation of substrate water molecules into the cluster as bridging of oxo groups as the proposed mode for activation of substrate. In each mechanism, two structurally equivalent oxo - atoms couple to form dioxygen upon clusters rearrangement to reform the starting cluster. In 1990 a triangular manganese cluster $[Mn^{IV_3} (O_4) (bipy) {}_4Cl_2]^{2+}$ was isolated by Girerd *et al.* (6) Another same type of triangular unit $[Mn^{IV}_3 (O_4) (bipy)_4]$ (H_2O_2) 2]⁴⁺ was prepared by Brudvig. (7) These two complexes show two types of Mn - Mn separation i. e., 2.7 Å and 3.3 Å comparable to those found in OEC, but the EXAFS spectrum is quite different from the OEC.

In 1993, Proserpio et al. proposed a model for photosynthetic oxygen evolution, based on a "hybrid" of the Berkeley "dimer of dimers" model and an experimental structure of a Mn (II, 3III) tetramer. (8) A family of manganese dimer [Mn^{IV} (salpin) (µ-O)]2 was prepared by Pecoraro et al. (9) This complex structurally resembles a part of the OEC Mn - assembly, as it has Mn - Mn distance 2.7 Å, precisely the distance deduced for the Mn - Mn separation in the lower S - state of the enzyme. This dimer has proven particularly useful for the studies of the manganese chemistry related to the function of the OEC. This complex is also a very competent catalase mimic and catalytically disproportionates to hydrogen peroxide. This is interesting in light of the possible centered catalase like reaction of the OEC. Another key aspects of this system has been its ability to protonate the oxo - bridges of the compound, and consequently to probe changes in the physical properties of this system. With this ligands and derivatives there of, a family of Mn dimer was prepared and they showed a broad range of pK_a 's for the protonation of the oxo - bridges and there also a broad range of reduction potential, which indicates how nature may easily be able to control the potential at the tetranuclear manganese cluster of the OEC. Magnetic susceptibility studies have shown that successive protonation of the two oxo - bridges reduces the coupling of the two manganese centres to one another. Furthermore, these protonations lead to a lengthening of the Mn - Mn vector in the complex. Recent advanced studies in OEC suggest that the successive oxidation of the OEC may occur via a hydrogen atom abstraction process, thus coupling the removal of an electron with a concurrent loss of a proton, possibly from a water bound to one of the manganese ions in the OEC, and it has been also found that the H atom abstraction is conducted by tyrosine (Y_z) , the electron transfer agent between the OEC and chlorophyll. The system [Mn^{IV} (salpn) (μ -O)]² was utilised to explore the feasibility of the H atom abstraction from the protonated

oxo - bridges of these complexes and experimental data suggest that such process is possible.

In 1994, Girerd *et al.* (10) isolated and characterised a tetranuclear cluster $[Mn_4 (O)_6 (bipy)_6]^{4+}$, model of S₃ state of the OEC and its one electron reduced from $[Mn_3^{IV}Mn^{III}$ (O) ₆ (bipy) ₆]³⁺ was also a good model of S₂ state. This tetramer is the closest model to Klein's model of the OEC.

Concerning the manganese chemistry, Brudvig, crabtree and coworkers, (11) reported that O_2 is evolved by the reaction of Mn^{II} and Mn^{III} mononuclear [Mn (L) O₂]ⁿ complexes containing the planer tridentate ligand terpyridine (n = +2)with potassium peroxymonosulphate (oxone, KHSO₅) in an acetate buffer solution at a pH lower than 4. This reaction produces a di - µ-oxo manganese mixed valent green coloured dimer [Mn₂^{III, IV}O₂ (terpy) ₂ (H₂O) ₂]³⁺ intermediate and it was reported that is dimer can catalyse water oxidation when sodium hypochlorite (NaOCl) is used as a primary oxidant. This was the first report of a di - μ -oxo complex, a structural model for the manganese complex in the OEC, which could carry out catalytic O-O bond formation. Yachandra et al. proposed a model of "dimer of dimer" for the OEC (Berkeley model) in which two di - µ-oxo dimanganese units, each with a Mn - Mn separation, of 2.7 Å, are connected via a single µ-oxo bridge to give a 3.3 Å Mn - Mn separation. The $[(Mn_2O_2) _ 2L_2]^{4+}$ complex (L= N, N. N'. N' - tetrakis (2 - pyridyl - methyl) - 2 hydroxylpropane - 1, 3 - diamine) by Chen et al. is the closest "dimer of dimer" model. In 2004, Brudvig and Crabtree reported the synthesis of a first unconstrained mono - μ-oxo bridged dimer of a pair of di - μ-oxo bridged Mn dimmer ($[Mn^{IV}_4O_5 (terpy) _4 (H_2O) _2]^{6+}$).

The di - μ -oxo and mono - μ -oxo bridged Mn–Mn distances of this complex are 2.74 and 3.51 Å respectively, which are close to the Mn–Mn separations of the OEC obtained from EXFAS studies.

Recent crystal structures by Zouni et al. (12) Kamiya and Shen (13) and Ferreira et al. (14) of the OEC of PS II at improved resolution have rekindled hopes among bioinorganic chemists of finally knowing the metal ion arrangement as well as the ligation environment of the Mn₄ cluster. In the recent crystal structure Ferreira et al. proposed a Mn₃Ca cubane core linked to a mono - oxo - bridged manganese centre for the active site. (14) This remarkably different geometry suggested by the authors with only marginally improved resolution compared to those for the previous two crystal structure is surprising. Furthermore, the structural changes of this multicluster PS II assembly when exposed to an X - ray beam over a prolonged period of time during data collection should also be considered. An obvious path to resolve these issues would be to obtain a structure of fully functional PS II crystal at a resolution where the exact positions of the Mn₄Ca core along with the surrounding ligands and cofactors can be accurately located. The plethora of knowledge gained from the Mn coordination chemistry described here in will certainly be extremely useful to prepare synthetic analogue of water oxidising cluster of PS II for the dark adapted state as well as for the other intermediate "S" - states.

The presence of a dinuclear core in the Mn catalase makes it of particular interest to biomimetic chemists. The speculative models structures utilise a single oxo - or hydroxo - ligand. Dismukes et al. (15) reported the first functional catalase model in 1987 which exhibit, high activity towards H2O2 disproportionation using a N - doner based septadentate ligand N, N, N', N' - tetrakis (2 methylenebenzamidazolyl) - 1, 3 - diaminopropane - 2 - ol binds with two Mn ions. EPR and UV - Vis spectroscopic investigations revealed that under the conditions of H₂O₂ decomposition both Mn^{III} - Mn^{III} and Mn^{II} - Mn^{II} oxidation states are present as observed for the natural manganese catalase enzyme. Another interesting system is [Mn₂ (2 -OHsalpn) $_{2}l^{2}$ (H₃ (2 - Ohsalpn) = N, N' - bis (salicylidene) -2 - hydroxy - 1, 3 - diaminopropane) which is unique in many ways and has allowed us to explore the chemistry of the catalase enzyme. This system allows one to produce a series of complexes in four different overall oxidation states with only minor structural changes. These dimer have been prepared in the Mn (II) Mn (II), II/III, III/III and III/IV oxidation states, a rare example of such a range of oxidation states with one ligand.

Sakiyama *et al.* explored various dinuclear manganese complexes as catalase mimics derived from 2, 6 - bis (N - [2 - dimethylamino) ethyl]iminomethyl - 4 - methylphenolate) and related ligants, and several intermediates were detected using various spectroscopic study like UV - Vis, mass spectrometry during H_2O_2 dismutase reactions.

Manganese complexes of 1, 4, 7 - triazacyclononane (tacn) or 1, 4, 7 - trimethyl - 1, 4, 7 - triazacyclononane (tmtacn) ligands were originally synthesised by Weighardt *et al.* (16) and studied as models for the oxygen evolving centre for PS II and for manganese catalase. The [Mn₂ (μ - O) ₂ (bisRpicX₂en) ₂] (R = H, Cl, NO₂; X = Me) complexes are known as both structural and functional models, and disproportionate H₂O₂ in aqueous media.

A significant breakthrough in catalytic efficiencies of manganese catalase mimics have been made recently. (17) The complex [Mn^{II} (bpia) (μ - OAc)]₂²⁻, {bpia= (bis ((2 - pyridyl) methyl) (1 - methylimidazol - 2 - yl) methyl) amine} can be considered a structural model for the catalytically active reduced form of manganese catalase because of its imidazole/acetate donor set. In the Mn^{III}Mn^{IV} oxidation level, the complex [Mn₂ (bpia) (μ - O)]₂²⁻ has been studied and is shown to be a catalase mimic, this is interesting because many other Mn^{III}Mn^{IV} dimer and the superoxidised Mn catalase are catalytically incompetent.

Research with biomimetic models has provided a wealth of information that has aided the interpretation of complex spectra, like those obtained from pulsed EPR experiments or XANES. Complete characterisation of series of models will allow us to probe relationship between structure and magnetic coupling or how structural modifications affect redox potentials of the bound metals. There is still much work that can be done in this ever - expanding field of study. Structural models have progressed from the more speculative prior to high resolution crystal structure analysis of the enzyme to the more corroborative. The corroborative modeling approach is intended to match the high resolution

data obtained for the active site of the enzyme. Spectroscopic models have thus for been used to elucidate magnetic electronic and structural properties of the enzyme. These models can be used to understand the reaction pathway by which the enzyme proceeds. Improved reactivity model complexes provided a unique way of testing mechanism in these manganese enzymes systems still a vast amount of time and effort has been devoted towards the synthesis and characterization of Mn - oxo complexes in order to better understand the structural and reactivity aspects of Mn - enzymes.

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