Coordination chemistry of manganese and iron with N,O-donor ligands: oxidation catalysis and magnetochemistry of clusters

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Manganese and Iron Complexes in Biomimetics, Oxidation Catalysis and Cluster Chemistry

1.1 Introduction

The purpose of this chapter is to give a general introduction on the rationale of understanding the coordination chemistry of manganese and iron in various subfields of chemistry. In the past two decades, there has been increasing interest in the coordination chemistry of manganese and iron with respect to their applications in biomimetic chemistry, oxidation catalysis and magnetism. Due to their central position in the periodic table, these metals can toggle easily between several oxidation states, giving rise to their versatile coordination chemistry. The catalytic properties mostly go hand in hand with their redox activity.

1.2 Manganese in Biomimetic Oxidation Chemistry

1.2.1 Manganese: General Introduction

The ever-increasing number of biomolecules found to contain manganese include manganese-containing superoxide dismutase (Mn-SOD), catalase, Mn-ribonucleotide reductase, Mn-peroxidase, ligninase, the oxygen evolving center (OEC) of photosystem II (PS-II), and Mn-thiosulfate oxidase. The mechanisms of action of these enzymes are very diverse and include oxo-atom transfer (WOC; the four-electron oxidation of water to dioxygen in PS-II, extradiol dioxygenase), electron transfer (SOD, catalase), the reduction of ribonucleotides to water and deoxyribonucleotides, and the oxidation of thiosulfate to sulfate.[1] Several advances have been made in the biomimetic structural and functional modeling by the synthetic chemists. Extensive synthetic studies for modeling the active sites of various manganese enzymes have added a wealth of knowledge to our understanding of

various aspects of manganese cluster chemistry with respect to structural, electrochemical and magnetic properties. This understanding has also helped in the development of manganese complexes with other actual applications in magnetic and catalytic chemistry.

1.2.2 Manganese Catalase

The principal mechanism of defense of living cells makes use of superoxide dismutase and catalase enzymes to protect the cell structure against harmful and reactive oxygen species, such as superoxide radicals or dihydrogen peroxide. Catalases are enzymes that protect cells from oxidative damage by scavenging the dihydrogen peroxide produced during dioxygen reduction.[2]

$$2\,H_2O_2 \rightarrow O_2 + 2\,H_2O \qquad \text{eq.1.1}$$

The catalases catalyze the disproportionation of dihydrogen peroxide as given in eq. 1.1. In addition to widely distributed heme-type catalases, a second class of relatively rare manganese catalases has been found in three bacteria, *Lactobacillus plantarum*,[4] *Thermus thermophilus*,[5] and *Thermoleophilium album*.[6] Crystal structures of the manganese core were determined for the reduced and/or the oxidized forms of the protein, *T. thermophilus* and *L. plantarum*.[7, 8] In general, a dinuclear active site is present in these Mn-catalases, possessing either a Mn^{II}–Mn^{II} or Mn^{III}–Mn^{III} dinuclear species bridged by a μ-(1,3)-carboxylate from glutamate and two μ-oxo or solvent bridges that electronically couple the metal centers (Figure 1.1A). One five-coordinate Mn site and one six-coordinate Mn site are present. The distance between the two manganese ions in the enzyme *T. thermophilus* in the reduced state was found to be 3.13 Å, while that in *L. plantarum* in the oxidized state was found to be 3.03 Å. The rate of dioxygen evolution by these enzymes is very high, i.e. of the order of 10^5 to

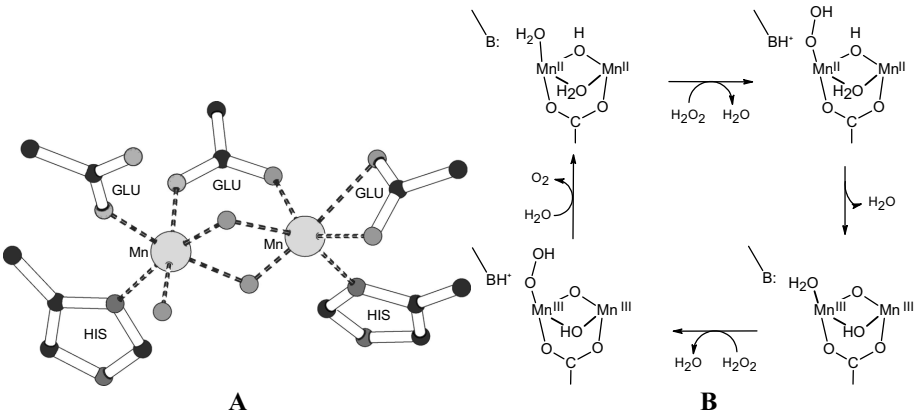


Figure 1.1: A: Core of the active site in *Lactobacillus plantarum* catalase. **B**: Proposed mechanism of H_2O_2 decomposition by manganese catalase.[3]

10^6 molecules per second.[9] The Mn···Mn distances derived from the EPR and EXAFS data provide complementary structural parameters with the Mn···Mn distances being 3.4 Å and 3.54 Å respectively,[10, 11] but are longer than that found crystallographically. The proposed mechanism of dihydrogen peroxide decomposition by these enzymes is given in Figure 1.1B.[3] The k_{cat}/K_M value for the rate of the decomposition of dihydrogen peroxide by the manganese catalase enzymes is higher than 10^6 $M^{-1}cm^{-1}$.[6, 9, 12] The potential relationship between manganese catalases and PS-II has been a strong driving force in the development of manganese catalase biomimetic chemistry. However, it is now realized that the manganese catalase is more close to the Mn-ribonucleotide reductase or Mn-arginase (both enzymes containing dinuclear manganese core as in Mn-catalases).[13]

Manganese catalase mimics

The first example of a structural and functional Mn-catalase mimic has been reported by Dismukes *et al*.: a dinuclear Mn(II) complex based on a septadentate ligand, *N*,*N*,*N'*,*N'*-tetrakis(2-methylenebenzamidazolyl)-1,3-diaminopropan-2-ol (benzimpn, Figure 1.2), which binds two Mn^{II} ions through an alkoxide oxygen from the 2-propanol backbone, a second bridging site occupied by either a chloride or a hydroxide anion.[14] The complex catalyzes disproportionation of 200 mmol of dihydrogen peroxide per millimole of complex before deactivation. When the chloride bridge is replaced by an acetate bridge, a lag phase is observed, and also excess of acetate inhibits the reaction, suggesting that the dissociation of

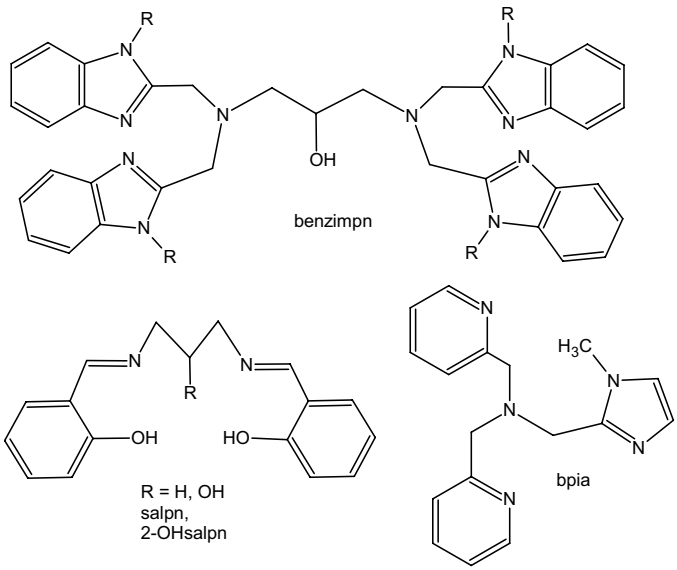


Figure 1.2: Structures of some of the ligands used for manganese catalase mimics

acetate prior to catalysis is critical to the reaction. In the absence of a coordination anion, the rate enhancement is observed with turnovers reaching 1000. Detailed spectroscopic and kinetic studies with the same ligand and bridging carboxylates revealed that the catalase catalysis proceeds through a ping-pong mechanism between the Mn^{II}_2 and Mn^{III}_2 states.[15-18] The best of these complexes gives a k_{cat} of 0.2 s^{-1}, but has k_{cat}/K_M values at about 3 $M^{-1}s^{-1}$.[15] It was also found that replacement of the μ-aqua bridge by a μ-hydroxo anion, by addition of a base (OH^-), eliminates the kinetic lag phase in the production of the product O_2 and increases the catalytic efficiency 240 fold.[15] With 5 eq hydroxide added to the system, the k_{cat} was 2.7 s^{-1}, a K_M of 6 mM for peroxide, and the catalytic efficiency, k_{cat}/K_M was 450 $M^{-1}s^{-1}$.[15] The k_{cat}/K_M value could be raised to 700 $M^{-1}s^{-1}$ by optimizing the solvent to an 11% methanol/89% water mixture.[15] It has been proposed that the added hydroxide binds intramolecularly to the catalytically active dinuclear manganese complex and is responsible for the deprotonation of metal-bound hydrogen peroxide, which is in turn, is essential for effective catalysis to occur.[15]

Pecoraro *et al.* have studied another important catalase mimic, the Mn-salpn (salpn = *N*, *N'*-bis(salicylidene)-1,3-diaminopropane) system that has been the model for fastest dihydrogen peroxide decomposition catalyst for several years.[19, 20] For the $[Mn^{III}$(2-OH-(X-sal)pn)$]_2$ (k_{cat} = 4-22 sec^{-1}) (2-OH-salpn = *N*,*N'*-bis(salicylidene)-2-hydroxy-1,3-diaminopropane) series,[20] the rates are lower than for the $[Mn^{IV}_2$(salpn)$O_2]$ (k_{cat} = 2500 sec^{-1}) system. The catalytic efficiency based on the k_{cat}/K_M for the $[Mn^{III}$(2-OH-(X-sal)pn)$]_2$ complexes, is in the range of 190-990 $M^{-1}s^{-1}$, which is a factor of 500-3200 smaller than the enzymatic rates. The Mn-salpn dinuclear complexes have been isolated and characterized in all relevant oxidation states and their reactivity is proposed to be analogous to the native manganese-catalase enzymes.[19-23]

The most efficient catalase mimic known to date is the $[Mn^{II}(bpia)_2(\mu\text{-}OAc)]_2(ClO_4)_2$ (bpia = bis(picolyl)(N-methylimidazol-2-yl)methylamine) system, which is a functional catalase mimic exhibiting saturation kinetics.[24] This complex is also a very good structural model for the reduced form of manganese catalase, because of its imidazole/acetate donor environment, but the Mn···Mn distance is 4.13 Å. The observed rates are exceptional with k_{cat} at 1.07 × 10^3 s^{-1} and k_{cat}/K_M 3.4 × 10^4 M^{-1} s^{-1}, making this complex the most efficient catalase mimic developed to date. These values are only a factor of 17-92 lower than to the three characterized manganese catalases, exceeding the activity reported for arginase disproportionation of dihydrogen peroxide.[3] However, the mechanism by which the reaction takes place has not yet been investigated.

1.2.3 Manganese Superoxide Dismutase (Mn-SOD)

The superoxide dismutases (SODs) catalyze the disproportionation of the superoxide ion (eq. 1.2) into dihydrogen peroxide and dioxygen. Production of Mn-SOD increases during the periods of oxidative stress, the activity of Mn-SOD is not inhibited by H_2O_2 and Mn-SOD has a significantly longer serum half life as compared to Cu,Zn SODs.[25] For these reasons Mn-SODs are regarded for (potential) treatment in a number of medical conditions arising from dioxygen damage to the tissue cells.[26-28]

$$2\,O_2^{\bullet -} + \; 2\,H^+ \rightarrow H_2O_2 + O_2 \qquad \text{eq. 1.2}$$

Crystal structures of Mn-SOD from *Thermus thermophilus*,[29, 30] *Escherelia coli*,[31] and human mitochondria[25] have been reported. The crystal structure of Mn-SOD from *T. thermophilus* in both oxidized and reduced forms reveals a trigonal-bipyramidal Mn^{III} ion coordinated to two N (histidine), and one O (asparatate) donors in the equatorial plane and another N (histidine) and an oxygen in the axial positions.[29, 30] The latter oxygen is a hydroxide ion in the oxidized structure, which compensates for the positive charge increase that occurs on oxidation of Mn(II) to Mn(III). The proposed catalytic mechanism is shown in Figure 1.3 and is relatively simple.[32] The superoxide anion binds to a vacant site on Mn(III), reduction to Mn(II) takes place, and a dioxygen molecule is evolved upon protonation of the OH group. A second superoxide anion binds to Mn(II), which is oxidized, and a proton transfers from the Mn(II) bound water molecule to the peroxide anion to form a hydroperoxo species. Dihydrogen peroxide release subsequently occurs upon protonation of the Mn(III)-hydroperoxo intermediate.

Manganese SOD mimics

Several manganese complexes have recently been proposed as structural and

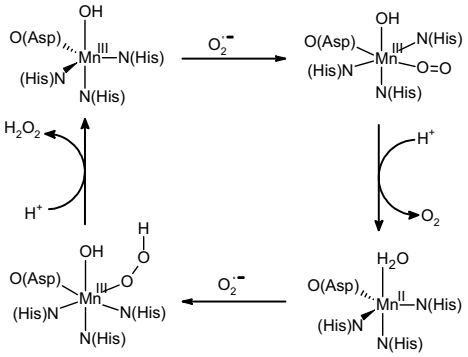


Figure 1.3: Superoxide dismutation mechanism for mononuclear Mn-SOD under physiological conditions.[32]

functional models of Mn-SOD. Manganese(II) complexes of sterically hindered tris(pyrazolyl)borate, $HB(Pz)^{3-}$ [33] (Figure 1.4) have been shown to be both structural and functional mimics of Mn-SODs having a distorted trigonal-bipyramidal structure with an apical nitrogen ligand as in Mn-SOD. Several four- and five-coordinate Mn(salen) (salen = N,N'-bis(salicylidene)-1,2-diaminoethane) complexes have also been shown to be excellent SOD mimics with the SOD activity lasting for over weeks.[33, 34] The complex Mn(2R,3R,8R,9R Dicyclohexano-1,4,7,10,13-pentaazacyclopentadecane)Cl_2 is the most active manganese SOD catalyst (k_{cat} = 1.21 × 10^8 $M^{-1}s^{-1}$ at pH = 7.4),[35] (Figure 1.4) functioning at a rate equivalent to native mitochondrial Mn-SOD enzyme.[36] The importance of conservation of the pseudo-octahedral geometry in the precursor Mn(II) complex resembling the six-coordinate octahedral geometry of Mn(III) regardless of the oxidation pathway involved, was proven by comparative studies on the stereoisomeric complex, Mn(2R,3R,8S,9S Dicyclohexano-1,4,7,10,13-pentaazacyclopentadecane)Cl_2 (showing no SOD activity).[35] Other complexes, including a few dinuclear manganese complexes, have been shown to give SOD activity.[35, 37-42] The SOD activity has been reported to be dependent on the redox potential of the metal center from studies on Fe and Mn substituted SODs.[43] The catalytic inactivity of Mn- and Fe-substituted SODs has been suggested to reflect redox potentials that are either lower (Fe-sub-(Mn)SOD) or higher (Mn-sub-(Fe)SOD) than those of native Fe- or Mn-SODs.[43, 44]

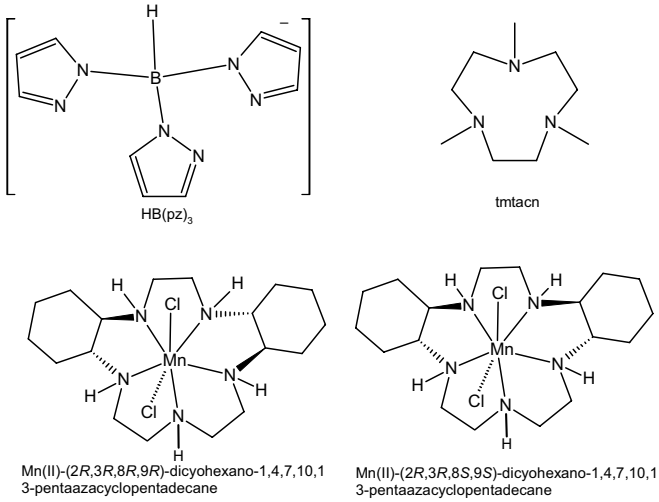


Figure 1.4: Structures of some of the ligands used in the synthesis of Mn complexes and manganese complexes for modeling of MnSOD.

1.2.4 The Manganese Cluster in Photosystem-II

The process of photosynthesis is the primary source of energy and carbohydrates to most life on earth. This reaction is initiated by the incidence of light on the special chlorophyll P-680 in the *trans*-membrane protein complex called photosystem-II (PS-II).

$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^- \qquad \text{eq. 1.3}$$

A tetranuclear oxo-manganese cluster, known as the oxygen-evolving center (OEC) is capable of oxidizing water to dioxygen, which is a four-electron and four-proton reaction, as shown in eq. 1.3. Inorganic co-factors such as Cl^- and Ca^{2+} ions are required for activity in addition to organic co-factors, such as tyrosyl radicals.[45-47]

The functioning of the OEC can be monitored by measuring the dioxygen evolution with consecutive light flashes upon thylakoid membranes. The fact that every fourth flash produced high yields of dioxygen (O_2) led Kok *et al.*[48] to propose a cyclic mechanism for the OEC. Schematically (Figure 1.5A), two water molecules enter a cycle (the Kok cycle) and through intermediate S_0 to S_4 steps, formed by successive one-electron oxidations of the OEC, a molecule of dioxygen and four protons are released. The S_0 to S_4 states of OEC are generated by electron transfer to a P-680 via a redox-active tyrosyl radical. The manganese complex in OEC is thought to function as a charge accumulator, extracting four electrons from two oxide ions in a single well-defined step that connects the S_4 and S_0 steps. O_2 release accompanies this $S_4 \rightarrow S_0$ transition. In the absence of light, the S_1 and S_0 states are stable, but the metastable S_2 and S_3 states decay to S_1.

X-Ray analyses have recently provided further details of the structure of the OEC in PS-II.[49] The structure shows a cubane-like Mn_4CaO_4 cluster (Figure 1.5B) where a cubane-like cluster of three of the manganese ions each having three μ_4-oxo bridges, is

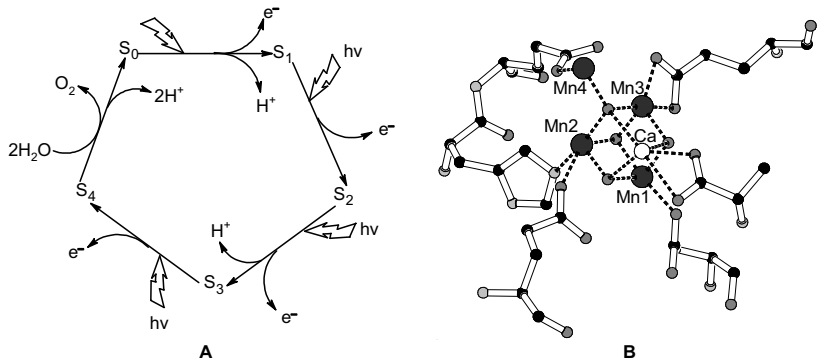


Figure 1.5: **A**: Schematic diagram of Kok's S-state cycle showing different oxidation steps leading to oxidation of water.[48] **B**:The oxygen evolving center of Photosystem II.[49]

connected to a fourth manganese ion through a single μ-oxo bridge. The distance between the Ca^{2+} ion from each of the manganese ions is 3.338-3.946 Å. Ca K-edge EXAFS data and Sr K-edge EXAFS data on PS-II samples have also indicated the possibility of Ca^{2+} being located within 3.3-3.4 Å from the Mn cluster in PS-II.[50, 51] The proposed oxidation states for the Mn_4 cluster in PS-II are as follows: S_0, (II, III, IV, IV); S_1, (III, III, IV, IV); S_2 (IV, III, IV, IV); S_3, (IV, IV, IV, IV), S_4, (IV, III, IV, IV).[52, 53] The mechanism of water oxidation into dioxygen is not understood yet. However, all mechanistic proposals involve water molecule binding at two neighboring Mn sites and then subsequent deprotonation steps followed by O–O bond formation.[53]

Manganese PS-II mimics

Much effort has been devoted to isolate Mn-oxo complexes with different nuclearities aided by various chelating (N and/or O) donor ligands. Extensive synthetic studies have been performed in order to obtain structural and/or functional models of the OEC including those by Wieghardt,[54-57] Brudvig and Crabtree,[58, 59] Christou,[60-63], Naruta[64, 65] and Armstrong.[66, 67] Several reviews giving excellent accounts on various structural models and mechanistic proposals have been published.[53, 68-73] Few examples worth mentioning here are those by Naruta *et al*. and Brudvig *et al.* Naruta *et al*. have reported evolution of dioxygen by a dinuclear Mn^{V}=O porphyrin complex in the presence of water.[64] Brudvig *et al.* have reported catalytic evolution of dioxygen by the complex $[(terpy)(H_2O)Mn^{III}(O)_2Mn^{IV}(OH_2)(terpy)](NO_3)_3$ (terpy = 2,2':6,2'-terpyridine) from either $KHSO_5$ (potassium oxone) or NaOCl.

1.3 Iron in Biomimetic Chemistry

1.3.1 Iron: General Introduction

The area of iron-containing biomolecules is very wide (more wide than manganese) and therefore, a small selection is given below. Three important iron-containing biomolecules attack substrates with aliphatic C–H bonds, namely P-450, Methane monooxygenase and Bleomycin. P-450 has a heme cofactor, which also serves as the active site for peroxidases, prostaglandin synthase and NO synthase.[74-79] Methane monooxygenase has a carboxylate-bridged diiron site, similar to those found in fatty acid desaturase and ribonucleotide reductase to generate its catalytically essential tyrosyl radical.[80] Bleomycin has a mononuclear nonheme iron center coordinated to five nitrogen ligands: an amidate, a pyrimidine, an imidazole, and two amines.[81] Each of these iron-containing biomolecules will be discussed briefly below.

1.3.2 P-450

P-450 can catalyze several different reactions, including C–H bond oxidations, epoxidations and de-alkylations.[76, 82] The enzyme is a monooxygenase, which means that it incorporates one atom of dioxygen into the substrate, while the other atom is converted into water. The heme iron(III) of P-450 has one cysteine as an axial ligand, and in its resting state, water or hydroxide is coordinated at the other axial site.[83] (Figure 1.6A) The generally accepted mechanism of the action of P-450 is given in Figure 1.6B.[84] The first step in the catalytic cycle entails the binding of the alkane substrate to the active site, which triggers the one-electron reduction of the iron(III) ion. The subsequent binding of O_2 to the iron(II) center forms an adduct analogous to oxyhemoglobin.[84]

The transfer of an electron and a proton to the active site generates an Fe^{III}–OOH species, strongly suggested by density functional calculations and EPR and ENDOR studies.[86, 87] Decomposition of this intermediate by O–O bond heterolysis affords a formally Fe^{V}=O or $[(Por^{\bullet})Fe^{IV}=O]^{+}$ species that is responsible for substrate oxidations.[76, 77] The high-valent intermediate can also be generated in the reaction of the Fe(III) enzyme with certain oxidants, such as iodosylbenzene, hypochlorite and peroxides, through a so called "shunt pathway" (Figure 1.6).[88]

1.3.3 Methane Monooxygenase

Methane monooxygenase (MMO) is an enzyme which has a carboxylate-rich non-heme diiron active site (Figure 1.7A).[89] The enzyme catalyzes the oxidation of methane to methanol with use of dioxygen. This unique reaction is the first step in the metabolism of methanotropic bacteria, which consume methane and dioxygen as their sole sources of carbon and energy. Oxygen binding to the diiron(II) enzyme generates two reactive intermediates that have been spectroscopically characterized: a (μ-1,2-peroxo)diiron(III) species and a

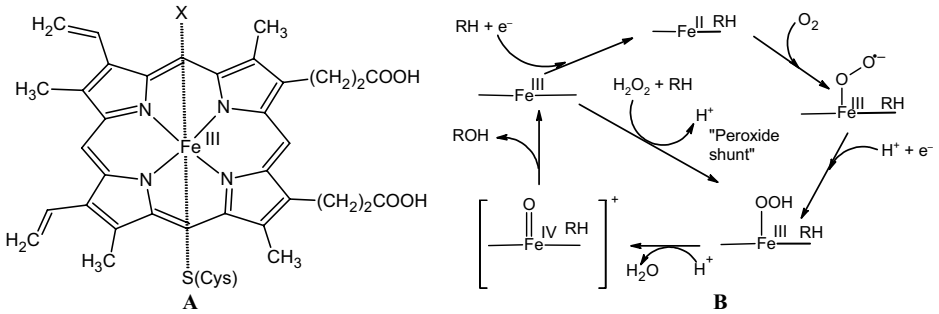


Figure 1.6: (**A**) Active site of P-450 (X = H_2O or OH^-),[83, 85] (**B**) Generally accepted mechanism of catalytic cycle of P-450.[84]

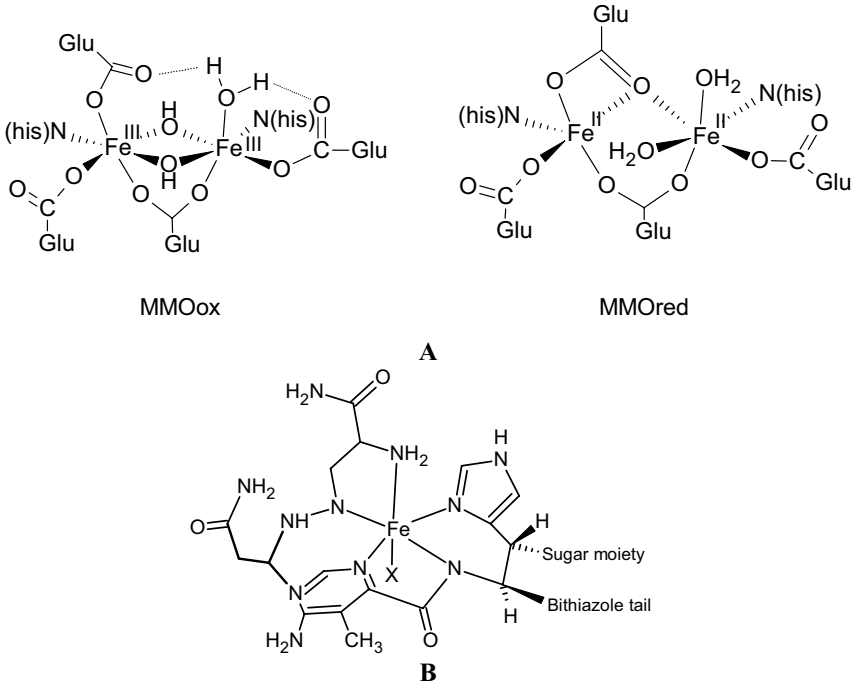


Figure 1.7: A: Active site structures of MMO_{ox} and MMO_{red},[80] **B**: Schematic representation of the structure of a part of iron bleomycin.[98]

diiron(IV) species with an $Fe_2(\mu\text{-}O)_2$ core.[90-94]

1.3.4 Bleomycin

Bleomycin is a low-molecular weight glycopeptide that in concert with iron(II) is effective as an antitumor drug (Figure 1.7B).[81, 95] Its antitumor activity is believed to arise from its ability to activate O_2 and to cleave DNA oxidatively in a double strand fashion. Upon injection of an electron and a proton, an intermediate called "activated bleomycin" is formed, which has been characterized as a low-spin Fe^{III}–OOH species.[95, 96] Subsequent O–O bond lysis results in the oxidative cleavage of the target DNA. The precise nature of the oxidant remains under discussion, but it is clear that there are both O_2-independent and O_2-dependent pathways by which the DNA is cleaved.[81, 97]

A large number of iron complexes have been studied that mimic the activity of these iron containing biomolecules. These will be reviewed briefly in section 1.4.7.

1.4 Manganese and Iron in Biomimetic Oxidation Catalysis

1.4.1 Introduction

The ultimate challenge of biomimetic catalysis is to develop systems that use O_2 as the oxidant, and perform oxidations in efficient way just like nature carries out most oxidations. For practical purposes, dihydrogen peroxide is often used as an environmentally friendly oxidant that does not need an external reductant (as is necessary with the use of O_2 as an oxidant).

Extensive amount of research has been devoted to this topic in the past 20 years with considerable achievements and understanding of the biomimetic systems. In this section a selection of the most important manganese and iron oxidation catalysts is reviewed.

1.4.2 Mn(salen) catalysts

In 1990, Jacobsen and Katsuki independently reported highly selective (> 99% ee) asymmetric epoxidation (Figure 1.8A) of alkenes using Mn(salen) catalysts.[99, 100] Since then, the area of Mn(salen)-mediated epoxidations has expanded greatly. This interest in the Mn(salen) systems is due to its utility as well as the intriguing mechanism in terms of catalytic cycle and mode of reaction of active species.

Also, ligand precursors with a wide range of substituents are easily available, either synthetically or commercially and thus the ligand structure can be easily varied. With regard to the origin of high enantioselectivity imparted by these complexes, it is generally assumed that it is dominated by the steric interactions between the chiral Mn(salen) complex and the two prochiral faces of the olefin. In these systems the stereogenic centers can be positioned close to the metal center, which improves the transfer of chiral information to the product.

Iodosylbenzene and its derivatives,[99, 101] sodium hypochlorite,[102] and *m*-chloro-perbenzoic acid (mcPBA)[103] have been successfully used as oxidants. Dioxygen in combination with an aldehyde as reductant[104, 105] as well as dihydrogen peroxide[106, 107] can also be used as oxidants. Addition of a donor ligand such as N-methylimidazole (N-Meim) was found to be crucial when dihydrogen peroxide is used as oxidant; a possible explanation is that the coordination of the donor ligand is crucial to the O–O bond cleavage of the intermediary hydroperoxide species [$HO–O–Mn^{III}$].[106, 107]

Bulky and/or chiral C3 and C3' substituents in the salen ligand, although not chiral, have been proven to be essential for the realization of high enantioselectivity (Figure 1.8B).[99, 102] *Cis*-olefins are generally better substrates than *trans*-olefins. Enantiofacial selection of *cis*-olefins is preferentially controlled by the chirality at C1" and C2" and that of *trans*-olefins

by the chirality induced by C8 and C8' (Figure 1.8 C and D).[99, 100, 102, 108] Complexes with an electron-donating group at the 5 and 5' positions exhibit higher asymmetric induction, but result in low yields, while complexes with electron-withdrawing groups at the 5 and 5' positions exhibit lower asymmetric induction, but higher yields.[109]

The ability of additional nitrogen- and oxygen-donor ligands to influence the outcome of metal(salen)-mediated epoxidations has been known since the initial work by Kochi and co-workers.[113, 114] Added ligands such as pyridine-N-oxide (PyO) were proposed to coordinate to the metal center and thus affect the outcome of the reaction.

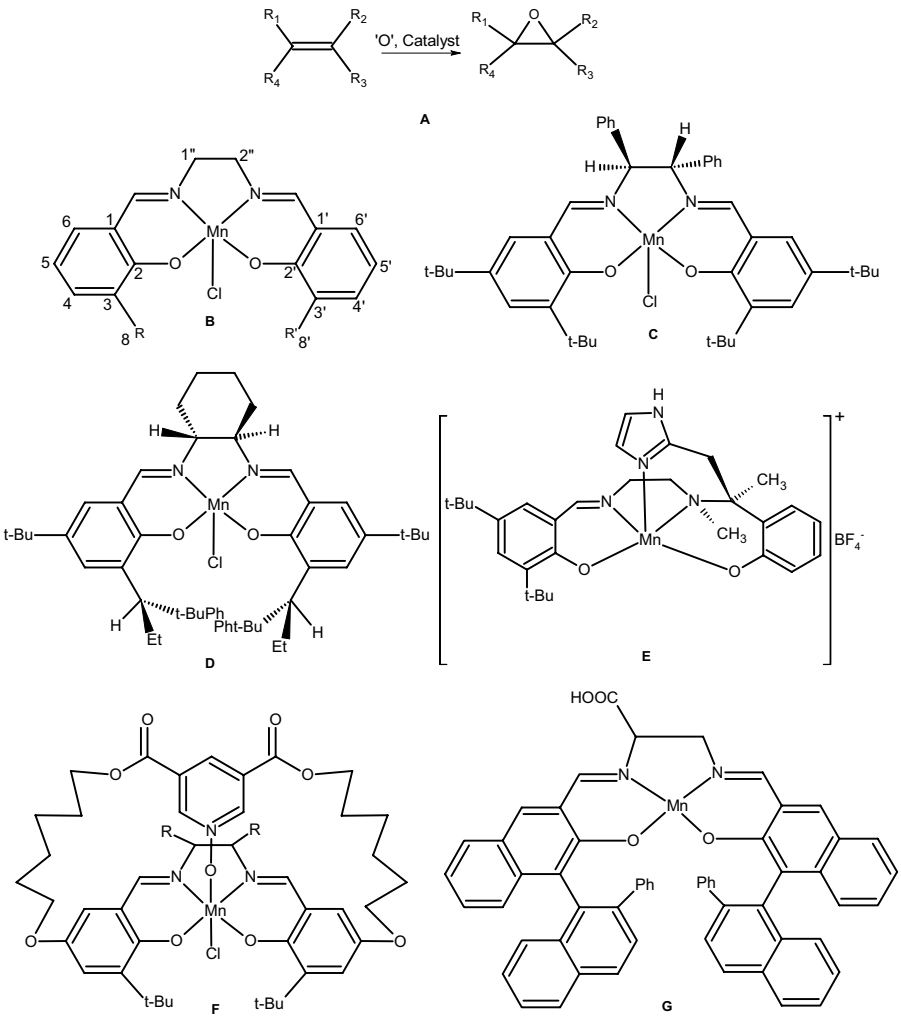


Figure 1.8: A: The epoxidation reaction. **B**: Structure of a typical Mn(salen) complex, **C** and **D**: Jacobsen's Mn(salen) catalysts,[99, 102, 109] **E**: Berkessel's imidazole tethered Mn(salen) complex,[110] **F**: Jacobsen's PyO tethered Mn(salen) complex,[111] **G**: Katsuki's conformationally fixed Mn(salen) complex.[112]

Berkessel and co-workers reported asymmetric epoxidations using a pentadentate Mn(salen) complex with a tethered imidazole moiety (Figure 1.8E) using dihydrogen peroxide as oxidant.[110] With 1,2-dihydronaphthalene as substrate and 10 mol% of catalyst, enantiomeric excess (ee) up to 64% were achieved. Control experiments using a tetradentate chelate lacking an imidazole donor showed that the pentacoordination of the manganese ion is crucial for catalytic activity as well as for enantiomeric excess.

Jacobsen *et al.* have synthesized a Mn(salen) catalyst with a built-in PyO module (Figure 1.8F) and produced evidence that the donor ligand must be bound to the complex during the formation of both C–O bonds in the product.[111] A Mn(salen) complex with a built-in donor ligand up in the form of a conformationally fixed carboxylate group reported by Katsuki *et al.* was found to be particularly effective as a catalyst with high asymmetric induction (Figure 1.8G).[112] The effectiveness of this catalyst and the variation of the effect of donor ligand with the catalyst structure have been rationalized in terms of an (salen)Mn=O species having a non-planar salen conformation.[115, 116]

Feichtinger and Plattner studied the effect of additives such as PyO using electrospray mass analysis (ESI-MS) and found that the donor ligand (PyO) rendered (salen)Mn=O species more reactive.[117] In contrast to earlier work, in their studies the additives were found to promote the formation of μ-oxo dinuclear species in solution.

Pietikainen studied asymmetric epoxidation of olefins using carboxylate salt as co-catalysts in the presence of aqueous dihydrogen peroxide, or the anhydrous urea-dihydrogen peroxide oxidant.[118] Electron-donating substituents at the 5 and 5' positions on the salen ligand result in higher asymmetric induction and longer lifetime of the catalyst. On the other hand, electron-withdrawing substituents accelerate the epoxidation reaction, but the enantioselectivity was considerably lower. The use of carboxylic acids instead of the corresponding carboxylate salts resulted in considerable retardation of the reaction rate. As good enantioselectivity was also observed using carboxylate salts that cannot coordinate to the metal ion, the author proposed that 'bacisity is a sufficient property of the additives in salen-catalyzed reactions.[118] Several simple salts were studied as additives, all giving good yields of epoxides with moderate to excellent enantioselectivity. Similarly high enantioselectivity (>99% ee) was also observed by Kureshy *et al.* in the epoxidation of chromene and indene, using ammonium acetate as co-catalyst and a dinuclear Mn(salen) complex as catalyst, where two mononuclear Mn(salen) units are bridged by a CH_2 substituent on the 5' position of one of the phenyl rings on the salen ligand.[119]

1.4.3 Mn-porphyrins

Manganese-porphyrin complexes are mainly studied for oxidation of alkenes and alkanes as structural and functional models of the P-450 enzyme. Investigations initially were directed at regioselective epoxidations with simple porphyrins, such as tetraphenylporphyrin (TPP) and tetramesitylporphyrin (TMP).[121-125] The early catalysts suffered from rapid catalyst deactivation by oxidative complex degradation, which resulted in the development of more stable "second- and third-generation" porphyrins with halogen, nitro or sulfone substituents (Figure 1.9).[85, 120, 126, 127] Mansuy and coworkers discovered the effectiveness of the Mn-porphyrins in the epoxidation of alkenes using dihydrogen peroxide as oxidant. The use of halogenated porphyrins improves the catalyst stability, and additives such as imidazole[128-130] or a combination of imidazole and carboxylic acids were used to ensure high reactivities.[131, 132] In addition, Mn-porphyrins containing tethered imidazole or carboxylic acids were also found to have enhanced reactivity.[133, 134] Imidazoles were proposed to coordinate to Mn throughout the reaction while carboxylic acid was proposed to cleave the peroxide O–O bond leading to a reactive Mn-oxo bond.[135] The Mn(V)-oxo species are well-established intermediates in Mn-porphyrin catalyzed epoxidations with dihydrogen peroxide.[136-138] Several other additives including ammonium acetate, amine N-oxides, and sodium hydrogen carbonate have also been investigated and their effect was comparable to those of imidazoles or carboxylic acids.[139-141]

1.4.4 Manganese-Me_3tacn Complexes and Derivatives

Interest in Me_3tacn-derived (1,4,7-trimethyl-1,4,7-triazacyclononane) catalysts for alkene epoxidation with dihydrogen peroxide originates from work at Unilever on potential detergent additives to oxidize the organic staining materials.[142-145] The $(\mu\text{-O})_3$ bridged complex $[(Me_3tacn)_2Mn^{IV}{}_2(\mu\text{-O})_3]^{2+}$ (Figure 1.10, complex **1**) is an example of one of these catalysts. Initially the complexes showed high rates of dihydrogen peroxide decomposition in

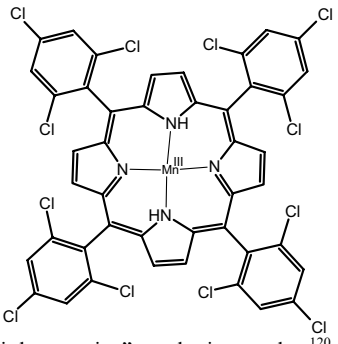


Figure 1.9: $[Mn(Cl_8tdcpp)]^+$, a "third generation" porphyrin complex.[120]

aqueous media. By decreasing the amount of dihydrogen peroxide[145] or by carrying out the reactions in acetone at 0 °C, product yields based on dihydrogen peroxide could be increased.[146, 147] An oxomanganese(V) intermediate has been detected with mass spectroscopy during phenol oxidations using the complex **1** although it is not clear if this species is responsible for catalytic activity.[148] Catalytic amount of an oxalate/oxalic acid buffer or sodium/ascorbate is reported to enhance the catalytic properties of Mn-Me_3tacn complexes for epoxidation reactions with dihydrogen peroxide in acetonitrile.[147, 149]

The most remarkable result was obtained in the epoxidation of methyl acrylate using sodium ascorbate (8 eq) as an additive: 0.03 mol% catalyst was sufficient for full conversion of the substrate (more than 3000 catalyst turnover numbers). It has been suggested that the addition of a catalytic amount of the didentate oxalate ligand prevents the formation of μ-peroxo-bridged dinuclear species and as a result the catalase-type decomposition of dihydrogen peroxide, often associated with dinuclear complexes, is suppressed.[151] Use of activated carbonyl additives, such as glyoxalic acid methyl ester methyl hemiacetal ($CH_3OCHOHCO_2CH_3$) in combination to the catalyst **1**, results in the production of high amounts of vicinal *cis*-diols in addition to epoxides.[152] Recently, tuning of the *cis*-hydroxylation and epoxidation activity using carboxylic acids in combination with the catalyst **1** has also been reported.[150] Spectroscopic studies and X-Ray analysis show that the control arises from the *in situ* formation of carboxylate bridged dinuclear complexes such as $[Mn^{III}_2O(CCl_3CO_2)_2(Me_3tacn)_2]^{2+}$ (**2**) and $[Mn^{II}_2(OH)(CCl_3CO_2)_2(Me_3tacn)_2]^{+}$ (**3**) (Figure 1.10). Tacn complexes can be very effective for epoxidations, but their synthesis is very difficult, and therefore the development of alternative systems with similar coordination environment (polyamine ligands), yet giving highly active catalysts, is an interesting challenge.

1.4.5 Other Mn Complexes

Feringa and coworkers have designed a hexadentate dinucleating ligand tptn (tptn =

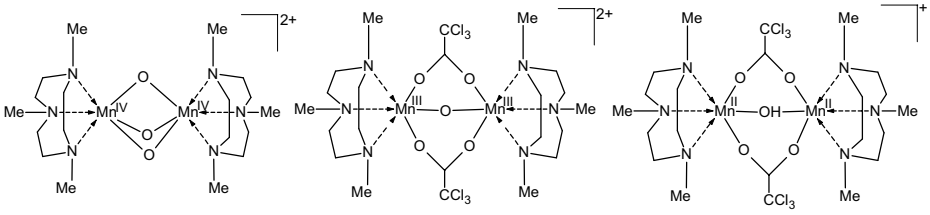


Figure 1.10: Schematic structure of dinuclear manganese complexes that can be formed with the ligand Me_3tacn ligand under different synthetic conditions.[150]

N,*N*,*N*',*N*'-tetrakis(2-pyridylmethyl)-1,3-diaminopropane) containing a three nitrogen donor set for each manganese site (Figure 1.11).[153] *In situ* studies using this ligand in combination with $MnSO_4$ at 0 °C in acetone, resulted in up to 900 turnovers in the oxidation of cyclohexene using dihydrogen peroxide as oxidant.

A manganese complex of the tetradentate ligand, *R*,*R*'-mcp, (*R*,*R*'-mcp = *N*,*N*'-dimethyl-*N*,*N*'-bis(2-pyridylmethyl)-1*R*,2*R*-diaminocyclohexane) (Figure 1.11), $[Mn^{II}(R,R\text{-mcp})(CF_3SO_3)_2]$, can rapidly (< 5 min) epoxidize a wide range of olefins at room temperature with low catalyst loadings using 1.2 equiv of peracetic acid.[154] Efficient disproportionation of dihydrogen peroxide by the complex precludes its use as an effective oxidant, but in the presence of peracetic acid the complex was found to perform selective epoxidations with turnovers up to 990 in the epoxidation of cyclooctene in acetonitrile.

A very simple system comprising manganese(II) sulfate and a carbonate buffer has been reported for the epoxidation of olefins by Lane *et al*.[155] Catalytic experiments were performed in DMF or tert-butyl alcohol as solvents and with the slow addition of a mixture of dihydrogen peroxide and aqueous 0.2 M sodium hydrogencarbonate buffer. Hydrogencarbonate is an essential part of this system; it forms a peroxymonocarbonate (HCO_4^-) ion. The presence of the intermediate was observed by ^1H NMR on mixing dihydrogen peroxide and HCO_3^-. The formed HCO_4^- reacts with manganese to produce the active epoxidation reagent (Figure 1.12). EPR studies have shown that manganese(II) is initially consumed during the reaction, and is regenerated towards the end of the reaction when dihydrogen peroxide is spent. This implies that Mn(II) is oxidized to Mn(IV) during the oxidations and then reduced back again to Mn(II), and that these salts do not simply act as Lewis acids.

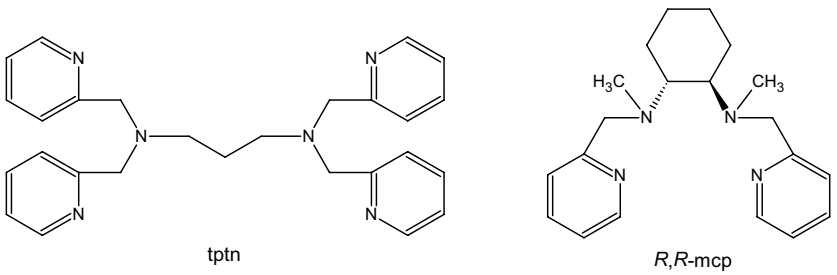


Figure 1.11: Schematic drawing of the ligands tptn and *R*,*R*-mcp.

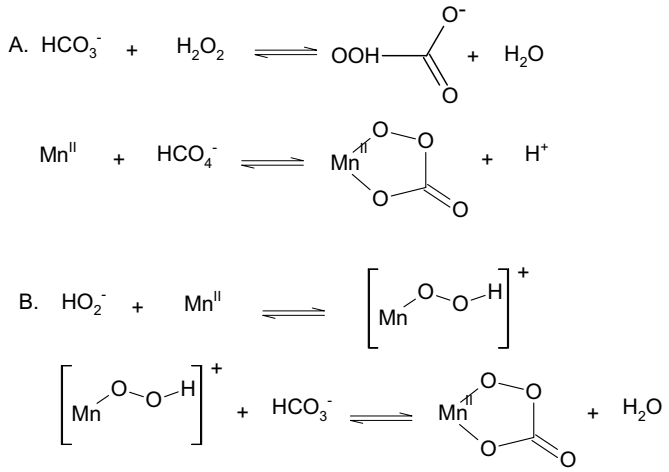
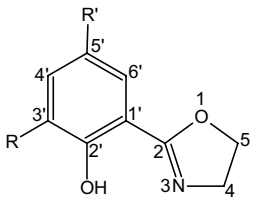


Figure 1.12: Formation of the peroxycarbonate complex (A) by the direct reaction of peroxymonocarbonate and (B) by the reaction of a peroxy complex with hydrogencarbonate[155]

1.4.6 Manganese Catalysts Containing Phenol-oxazoline Ligands.

The manganese complexes based on 2-(2'-hydroxyphenyl)oxazoline (Hphox) ligand (Figure 1.13) have been developed by Hoogenraad *et al.*[156-160] The imine C=N bond of the oxazoline ligand has been reported to be more stable towards oxidative degradation than that of the corresponding C=N bond of the salen ligand.[161] The complex $[Mn(phox)_3]$ is an active epoxidation catalyst with dihydrogen peroxide as the oxidant; in acetone and at 0 °C, turnovers up to 220 were obtained in the epoxidation of styrene in 15 minutes. Benzaldehyde was found to be the major side-product obtained in these reactions.

Further studies using manganese complexes of substituted phox ligands were also performed. Using the $[Mn(5'\text{-}NO_2phox)_3]$ complex, turnovers up to 207 were obtained in acetone, and the catalytic activity continued for longer time (one hour). The prolonged activity has been associated with the higher stability of the catalyst due to the electron-withdrawing nitro group. Manganese complexes with electron-donating methyl and methoxy-substituted analogs of the phox ligand yield lower activity. The presence of a base such as imidazole was found to be indispensable for the catalytic reactions. Using ESI-MS analyses $[MnL_2]^+$ and $[MnL_2(N\text{-}Meim)]^+$ species were detected during the oxidation of styrene in methanol and acetone. Decomposition of the oxazoline group was also observed with ESI-MS analyses and indicates that catalyst degradation is the limiting factor for the catalytic activity.



Ligand	R	R'
Hphox	H	H
H-5'-NO_2phox	H	NO_2
H-3',5'-dClphox	Cl	Cl
H-5'-Clphox	H	Cl
H-5'-Mephox	H	CH_3
H-3'-Mephox	CH_3	H
H-5'-MeOphox	H	OCH_3

Figure 1.13: Structure of the Hphox ligand and derivatives.

1.4.7 Iron Complexes

Iron complexes have been studied extensively, mainly for catalyzing C–H hydroxylations; however, several of the complexes are also known to catalyze epoxidations and *cis*-dihydroxylations. Iron complexes in general show lower activity in catalytic oxidations as compared to their manganese analogs. However, these complexes have been studied extensively for mechanistic relevance of the oxidations catalyzed by P-450, bleomycin and MMO. Thus, most of the literature on catalytic oxidations by iron complexes involves mechanistic studies instead of purely catalytic studies.

The reactivity pattern for the substrate functionalization by iron complexes can proceed mainly *via* two reaction pathways: one by the Fenton reaction, involving the uncontrolled autoxidation by hydroxyl radicals, the other involving a metal-based oxidant formed by a decomposition of the Fe–OOH transient intermediate. To confirm the electronic nature of the actual catalyst intermediate, a few criteria are useful which include: (a) *Kinetic isotope effect* (KIE), (b) *alcohol to ketone ratio when using alkanes*, (c) *regioselectivity*, and (d) *retention of configuration* (RC).

The first report of the use of metalloporphyrin complexes as catalysts for epoxidations was by Groves *et al*. in 1979, using iodosylbenezene as oxidant.[162] A variety of iron-porphyrin complexes have subsequently been studied for catalyzing oxidations employing dihydrogen peroxide as oxidant for mimicking the activity of P-450.[85] However, due to poor stability and difficult synthesis of these catalysts, their applicability is limited.

The iron-tpa (tpa = tris(2-pyridylmethyl)amine) (Figure 1.14) family of complexes has been intensively studied by the group of Que.[84] The iron-tpa complexes catalyze a variety of oxidations such as C–H hydroxylations, epoxidations and also *cis*-dihydroxylations.[163, 164] Similar research was also extended to the family of the tetradentate ligand bpmen (bpmen = *N*,*N*'-bis(2-pyridylmethyl)-*N*,*N*'-dimethyl-1,2-diaminoethane) (Figure 1.14).[165] The corresponding iron complexes show similar oxidation activity as the complexes based on tpa analogs.[164] The catalytic reactions carried out in the presence of $H_2{}^{18}O$ and H_2O_2 afford ^{18}O

containing stereospecific oxidation products, indicating that the oxidant responsible for stereospecific alkane hydroxylation can undergo oxygen-exchange with water. This provided evidence for that a non-heme iron catalyst can hydroxylate alkane stereopecifically via a high-valent iron-oxo species.

Interestingly, in the iron-tpa chemistry the introduction of an additional CH_3 group at the 6-position of the pyridine ring was found to alter the course of epoxidation towards *cis*-dihydroxylation.[164] The catalytic behavior associated with these catalysts arises from the spin state of the Fe^{III}–OOH intermediate that reacts with the substrate in distinct ways. The introduction of the 6-methyl group on the pyridine ring favors the high-spin state for the iron center. This is due to the steric effects of the 6-methyl group that restrict the extent to which the metal-ion cavity can shrink, giving rise to the observed *cis*-dihydroxylation activity.

The iron complex of an amide-containing ligand, $[Fe(H_2bppa)(OOH)]^{2+}$, (H_2bppa = bis(6-pivalamide-2-pyridylmethyl)-2-pyridylmethyl)amine) (Figure 1.14), decomposes gradually in acetone at 20 °C and accelerates the rate of oxidation of cyclohexane to cyclohexanol selectively (only traces of cyclohexanone are formed).[166] The observed high selectivity reveals that free radicals and dioxygen that initiates non-selective radical chain oxidations do not participate in the oxidation reaction.

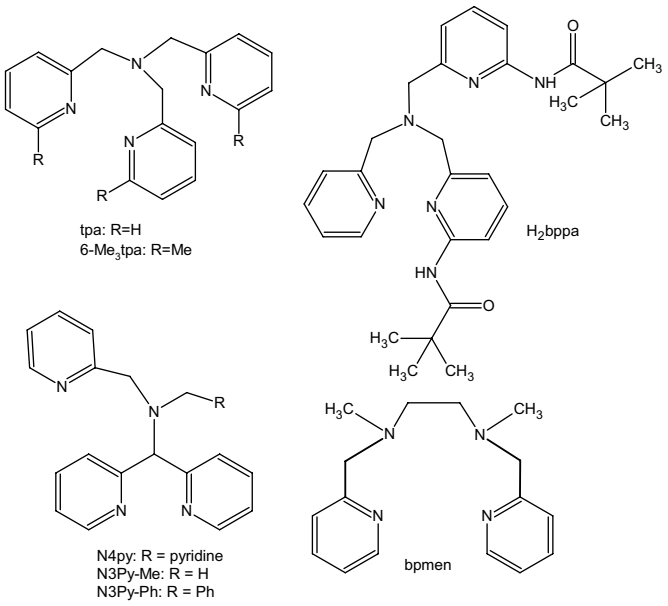


Figure 1.14: A selection of some of the ligands used for the synthesis of iron complexes for biomimetics and catalytic epoxidations.

Iron complexes of the pentadentate ligand N_4py (N_4py = *N*,*N*-bis(2-pyridylmethyl)-*N*-bis(2-pyridyl)methylamine) (Figure 1.14) have been studied as models for iron bleomycin.[167] The complexes catalyze the oxidation of several alkanes to the corresponding alcohols and ketones in a non-stereospecific way. On addition of dihydrogen peroxide a purple intermediate was observed similar to activated bleomycin, the active form of the drug.[168] This intermediate has been formulated as a low-spin iron(III) hydroperoxide complex. The oxidation of cyclohexene using the iron complex of N_4py resulted in the formation of the allylic oxidation products, the epoxide being a minor product. The results confirmed the importance of two, *cis* labile sites on the iron center in order to achieve stereospecific olefin epoxidations.[168]

Jacobsen and co-workers reported efficient catalytic epoxidations by the complex $[Fe^{II}(bpmen)(CH_3CN)_2](SbF_6)_2$[169] (Figure 1.14) in combination with acetic acid. It was suggested that a (μ-oxo)(μ-carboxylate) diiron(III) complex was generated during catalysis as confirmed by X-Ray analyses and ligand field spectroscopy. However this result is in disagreement with Que *et al*. who attribute the lack of activity of a (μ-oxo)(μ-carboxylate) diiron(III) complex to the presence of the carboxylate bridge, which would hamper facile coordination of H_2O_2.[164, 170]

1.5 Magnetochemistry of Manganese and Iron Clusters

The last few decades have witnessed an explosive growth in the interest in polynuclear manganese and iron compounds with primarily oxygen and nitrogen coordination. This has been mainly due to their relevance in two fields, namely bioinorganic chemistry and molecular magnetism. Clusters comprising manganese and iron ions are present in several metalloenzymes and metalloproteins ranging from the protein ferritin, responsible for iron storage,[171, 172] to the water oxidizing complex of Photosystem II for bacterial photosynthesis.[1, 53] In the magnetism area, manganese and iron clusters with high nuclearities and appropriate topologies may possess large ground spin values, and can function as single-molecule magnets (SMMs).[173-175]

The ability of a molecule to act as a SMM is of potential interest for future data-storage applications. Magnetic particles are used for digital information storage on hard drives, DVDs and other devices. There is great interest by high tech companies in increasing the density of information storage, which means increasing the number of bits of information in a given area of hard drive or other device.[176-178] To store more digital information in a given area, each magnetic particle must be smaller. The size of the particles must also be the

same so they will behave the same. SMMs have many important advantages over conventional nanoscale magnetic particles composed of metals, metal alloys or metal oxides. These advantages include uniform size, solubility in organic solvents, and readily alterable peripheral ligands, among others. These molecules are much smaller than the magnetic particles currently used in information storage, but nevertheless behave as magnets at only low temperatures. So each molecule can be considered an ultra-small magnetic particle, and this promises access to the ultimate high-density information storage devices.

In short, an SMM is magnetizable, because it has a potential energy barrier between its "spin up" and "spin down" states. Several experimental manifestations are known of the fact that a molecule has a significant barrier for magnetization reversal and thus is functioning as a SMM at low temperatures: (1) there will be a divergence between the zero-field cooled and magnetization at some "blocking" temperature; (2) the most classic indication is the observation of a hysteresis loop in the magnetization versus external magnetic field response;[179, 180] and (3) there will be a frequency-dependent out-of-phase AC magnetic susceptibility signal indicative of slow magnetization relaxation, because at low temperatures the magnetization of a SMM will not be able to keep in phase with an oscillating magnetic field.[181] The slow magnetization relaxation is due to the presence of an energy barrier to be overcome in the reversal of magnetic moment.[182] At the simplest level of approximation the relaxation time follows a thermally activated barrier:[183]

$$\tau = \tau_0 \exp(\Delta / k_B T) \qquad \text{eq. 1.4}$$

where Δ is the height of the barrier and τ_0 is the pre-exponential factor.

Such an SMM displays slow relaxation of its magnetization and functions as a magnet below its blocking temperature (T_B). The relaxation time of the magnetization, τ, is thermally activated and results mainly from the spin ground state (S_T) and the uni-axial anisotropy (D) of the molecule. In this regime, the theoretical energy barrier Δ is equal to $|D|S_T^2$ or $|D|(S_T^2 - 1/4)$ for integer and half-integer S_T, respectively. Thus it is important to develop molecules exhibiting large spins and/or large D values. To design and synthesize new nanomagnetic materials based on molecular clusters it is therefore necessary to achieve large S spin ground state. This can be done using a small number of ions if the individual components have a large spin. Manganese(III) clusters often display unusually large spin ground states, and negative D values arising from the presence of Jahn-Teller distortion.[174] Iron(III) clusters, on the other hand, usually give clusters with antiferromagnetic interactions between the metal centres. However, certain Fe_x topologies result in large ground spin states,

because of the occurrence of the spin frustration effects.[184] Spin frustration is defined here in its general sense as the occurrence of competing exchange interactions of comparable magnitude that prevent (frustrate) the preferred spin alignments.[184] Thus, in certain topologies the spins of two antiferromagnetically coupled metal ions may be forced into a parallel alignment by other, stronger interactions; frustrating the intrinsic preference of the spins to align antiparallel. An appropriate quantity and distribution of frustrated exchange pathways in some Fe_x topologies can lead to a significantly large value of the total molecular spin, even when all the pairwise Fe_2 exchange interactions are antiferromagnetic.[184]

The synthesis and structure of the first SMM was reported by Lis in 1980.[185] The compound is a Mn_{12} cluster of formula, $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]_2{\cdot}CH_3COOH{\cdot}4H_2O$. (Figure 1.15) The compound has a $S = 10$ ground state in ≥ 20 kG field. Several derivatives of the Mn_{12} cluster were prepared, and these Mn_{12} complexes were the first molecular species exhibiting a nonzero, out-of-phase component in their ac susceptibility response in zero applied field.[175, 186, 187] The relaxation time of the magnetization has been experimentally found to follow a thermally activated behaviour, with $\tau_0 = 2.1 \times 10^{-7}$ s and $\Delta / k = 62$ K.[186] A variety of experimental procedures have been developed in the past decade to rationalize the geometry, nuclearity and topologies of Mn, Fe clusters. Although many efforts have been made to increase Δ and τ_0, the first family of SMM of general formula $[Mn_{12}O_{12}(OR)_{12}(H_2O)_4]$ so far still displays the highest blocking temperatures.

The family of SMMs has grown considerably over the past few years. Most of the

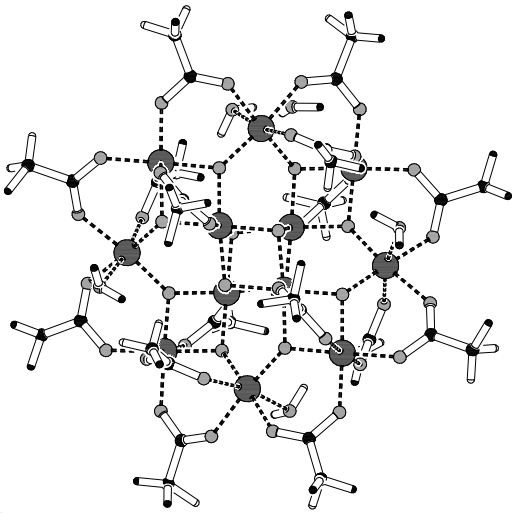


Figure 1.15: A PLUTON view of molecule of the complex $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]_2{\cdot}CH_3COOH{\cdot}4H_2O$.[185]

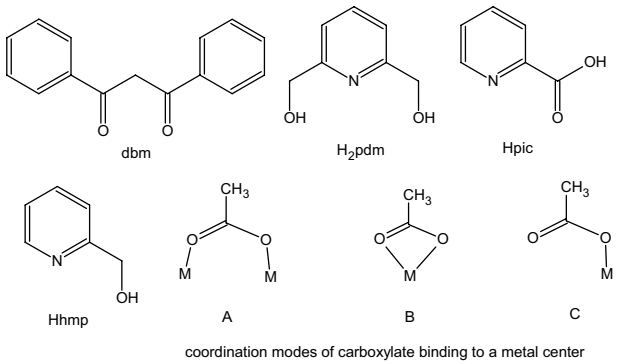


Figure 1.16: Schematic drawings of the ligands used for the synthesis of manganese and iron clusters and bonding modes of carboxylate groups

exciting new examples are found in manganese chemistry such as Mn_4,[188-190] Mn_6,[191, 192] Mn_{11},[191] Mn_{12},[186] Mn_{16},[193] Mn_{18},[194] Mn_{22},[195] Mn_{25},[196] Mn_{26},[197] Mn_{30},[198, 199] and Mn_{84}.[200] SMMs with iron have also been reported, such as Fe_4,[201] Fe_8,[201] Fe_{10},[202] and Fe_{19}.[203]

The ligands used for synthesis of these clusters can be chelating or bridging, usually with "N,O", or all 'N' or all 'O' coordination. Some of the ligands that have been extensively studied from this point of view include (Figure 1.16); Hdbm, (dibenzoylmethane)[204-207] Hhmp, (2-(hydroxymethyl)pyridine)[208-211] H_2pdm, (pyridine-2,6-dimethanol)[212, 213] and Hpic (picolinic acid)[214, 215]. The most dominating ligands that have given rise to isolation and characterization of an enormous amount of clusters are the simple carboxylate ligands (mainly acetate) due the variety of bridging and coordination modes that are possible for these type of ligands.[210, 216-219] Although use of the carboxylates poses a major drawback that the topologies and oxidation states can be hardly controlled, a wide variety of clusters have resulted from the reaction using carboxylate salts with manganese and iron. In addition, by reactions in air, oxide/hydroxide ions from air or water get incorporated frequently in these compounds and facilitate the formation of novel varieties of topologies and geometries around the metal center.

1.6 Objectives and Outline of the Thesis

The synthetic and characterization studies on manganese and iron complexes containing mainly N,O donor ligands lead to their use in a variety of applications including biomimetics, catalysis and magnetochemistry. The aim of the research described in this thesis is the synthesis, understanding of the coordination chemistry and the investigation of their interaction with dihydrogen peroxide. Due to the main interest of possible applications of the

complexes in oxidation catalysis, interaction with dihydrogen peroxide has been particularly investigated.

In bulk chemistry, stoichiometric reagents, *viz.* K_2CrO_7, $KMnO_4$ and derivatives are usually applied in catalytic oxidations.[220-222] However, the use of these reagents has two major disadvantages: it results in high chemical costs and a stochiometric amount of (often toxic) inorganic salts as waste is formed.[220, 221] Homogeneous catalysis seems to be the perfect alternative, since it ideally involves mild conditions, employs efficient oxidants, such as O_2 or H_2O_2 and allows for a good tuning of the catalyst, resulting in selective reactions.[223]

The $[Mn(R\text{-}phox)_n]$ complexes developed in Leiden, show good activity in the epoxidation of styrene, with turnovers up to 200.[156] Using ESI-MS analyses $[Mn(L_2)]^+$ and $[Mn(L_2)(N\text{-}Meim)]^+$ species have been detected during the oxidation of styrene in methanol and acetone. Decomposition of the oxazolines group was observed with ESI-MS analyses and indicates that catalyst degradation is the limiting factor for the catalytic activity. A substituted phox ligand containing an electron-withdrawing nitro-group was found to show activity for a long time. The prolonged activity has been associated with the higher stability of the catalyst due to the electron-withdrawing nitro group.

Recently, Ito *et al*. reported a carboxylate substituted Mn(salen) catalyst, which resulted up to 9,200 turnovers and 99% ee in the epoxidation of 2, 2-dimethylchromene derivatives.[112] Therefore, the ligands Hphox-COOR (R = H, CH_3) (Figure 1.17) containing electron-withdrawing carboxylate or ester groups have been synthesized in the present work and their manganese and iron complexes have been studied in catalytic epoxidations. In order to better understand the catalysis, interaction with N-Meim in solution has also been studied.

The ligand, HMesalim (Figure 1.17) a precursor for the synthesis of the HphoxCOOR ligands contains an imine group. The presence of such a hydrogen atom could give rise to potential hydrogen bonds with the oxidant during catalysis. Therefore, the manganese and iron complexes of this precursor ligand have also been synthesized and their interaction with dihydrogen peroxide has been studied. During the synthesis of mononuclear manganese and

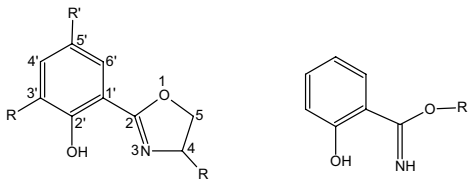


Figure 1.17: Schematic drawings of the ligands studied in this thesis.

iron complexes with this ligand a variety of oligonuclear clusters have been isolated. Magnetochemistry of these complexes has been studied for their potential applications as nanomagnets.

The outline of the thesis is as follows:

In the second chapter the synthesis, characterization and catalase activity of manganese complexes of the ligand HMesalim and HEtsalim (methyl and ethyl salicylimidate respectively) are discussed. Chapter 3 describes the synthesis, characterization and catalytic activity of manganese complexes of the phoxCOOR ligands. Chapter 4 deals with the synthesis, characterization and catalytic activity of iron complexes of the phoxCOOR ligands. The synthesis and magnetochemistry of oligonuclear manganese and iron compounds are described in Chapter 5. In the final chapter the concluding remarks and future prospects are discussed. Parts of this thesis have been published,[224-226] or have been submitted for publication,[227] or are in preparation.[228, 229]

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